ENVIRONMENTAL CONSEQUENCES ASSOCIATED WITH ASH-STABILISATION OF ORGANIC SLUDGES FROM THE SYNTHOL PROCESS

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To my Mother.

The gift you have given me is more than words can describe

Ukhule uze ukhokhobe

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ABSTRACT

Worldwide increases in environmental awareness have led to the development of new innovative technologies aimed at site remediation and hazardous waste treatment. Solidification/Stabilisation (S/S) is one of such technologies and it has emerged as an environmentally acceptable treatment option for hazardous waste. Initially applied to inorganic wastes, S/S is now being investigated for the treatment of organic wastes and sludges.

Challenges facing this venture into the S/S of organic wastes include the lack of technical information on waste-binder interactions, the uncertainty regarding an appropriate method to evaluate the performance of CFS systems, as well as evaluation of the long-term stability of stabilised material.

This paper attempts to expand the understanding of chemical and micro-structural waste-binder interactions. Also addressed is the weathering behaviour of stabilised/solidified organic waste when exposed to two different leaching media, distilled water and the US EPA's Toxicity Characteristic Leaching Procedure (TCLP) solution. Addressed to a minor extent is the effect of stabilised/solidified organic waste on biomass production of sweetcorn maize.

The focus in this study was the stabilisation of the synthol sludge (synthol gunk) using a pozzolan system. This was done by preparing stabilised waste forms from synthol gunk and fine ash (ash obtained from the slimes dams, hence has hydrated to some extent). A particle size fraction less than 2 mm of these waste forms were leached with the two leaching solutions. Some of the material was pressed into pellets, which were subsequently leached in the same leaching solutions. The pellets were analysed under SEM-EDS for micro-structural analysis.

In a separate set of experiments fine ash, synthol gunk and the stabilised waste forms were mixed with soil in the range 0% to 30% waste addition, after which sweetcorn maize was planted to study the effects on biomass production.

Other instrumental techniques used in this study include WDXRF, ICP-MS, FTIR, IC as well as the analysis of dissolved organic carbon (DOC).

The study showed that the trace metal speciation of the pozzolanic binder is affected by the presence of the organic waste, with a possible threat of turning the binder into a hazardous material. Elements that were leachable by TCLP on the stabilised product include B, Mn, Ni, Fe, and Br. The addition of lime in the system appears to lower the leachability of B, Mn, and Br while

worsening the leachability of Fe, Ba, and Zn.

However, addition of lime increases the leachability of B, Cr, Mn, Fe and Br in distilled water. The most likely source of B, Fe, Br and Ba is fine ash.

Plant growth studies showed that the toxicity threshold of synthol gunk in the stabilised material on biomass production appears to be lowered from about 2.5% in unstabilised synthol gunk to about 1.2% either due to synergy or the additive effect of ash and synthol gunk. Furthermore, it is likely that some of the toxicity of synthol gunk is due to the hydrophobic coating of roots resulting in inadequate water intake by the plant.

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ABBREVIATIONS

ANC	Acid neutralising capacity
ARL	Acceptable risk level
Ash	Fine ash from the ash dumps
ASTM	American Society of Testing and Materials
EEC	Estimated environmental concentration
GASH	One part synthol gunk to 6.67 parts ash
GLASH	One part synthol gunk to 6.67 parts LASH
LASH	Ten percent slaked lime in ash by weight
SEM-EDS	Scanning electron microscope coupled to energy dispersive spectrometry
S/S	Stabilisation/solidification
TCLP	Toxicity Characteristic Leaching Procedure
US EPA	United States Environmental Protection Agency
WDXRF	Wavelength dispersive X-ray fluorescence spectrometry
XRD	X-ray diffraction spectrometry

CHAPTER ONE

1. INTRODUCTION

A worldwide increase in environmental awareness has ultimately led to a constant increase in the disposal costs of hazardous waste. Waste generators are now opting for treatment processes to render their waste materials non-hazardous in a bid to minimise disposal costs. This practice has seen waste management becoming a financially attractive activity among companies world-wide, and now the race is on for the selection of the cheapest treatment process for a variety of projects which include meeting disposal permit requirements, site closure and ad hoc procedures.

Stabilisation / Solidification (S/S) was identified by the US EPA as one of the most affordable innovative technologies for site remediation and the treatment of a variety of hazardous wastes. However, its application was limited to inorganic waste for two main reasons:

* Inorganic wastes are the only really hazardous waste materials that cannot be destroyed by conventional thermal and biological techniques. A more reasonable approach was, therefore, to retard their mobility within an aqueous medium.

* Incineration and biodegradation were perceived as treatment options of choice when it comes to organic waste.

There is now a paradigm shift towards the treatment of hazardous organic wastes using the S/S technology. This is due to the realisation that some thermal techniques, to a certain extent, are changing the form of the waste material from liquid/solid to a gas phase, rather than truly treating the waste. Biodegradation, on the other hand, cannot be considered as a solution since some organic sludges prove very difficult to biodegrade on a practical time frame.

The S/S of hazardous organic wastes is still at a developmental stage with binders such as asphalt, modified clays and thermoplastic techniques utilising polypropylene and other organic binders being used. The organic binders appear to work well if properly chosen for a specific waste stream, but they usually require specialised instrumentation and should be conducted in a very well controlled manner. This raises their implementation and maintenance costs, which makes them less attractive.

The merits of using fly ash as a binder include the possibility of treating two waste streams at the same time since fly ash can also be considered as a waste stream and the availability of fly ash in large quantities in which the only major cost is transport. This is the field of S/S that is being currently investigated as one of the cheapest hazardous waste treatment options.

The evaluation of stabilised/solidified waste forms appears to be another area of S/S that has been met with uncertainty. Poon and Lio (1997) highlighted the limitations of the Toxicity Characteristic Leaching Procedure (TCLP), a standard leaching procedure developed by the United States Environmental Protection Agency (US EPA), in the evaluation of stabilised/solidified waste forms that have a high acid neutralising capacity. They pointed out that the TCLP test does not extend to evaluate the effects of a waste that has its acid neutralising capacity exhausted by exposure to acid conditions for prolonged periods of time.

On the other hand, some leaching tests require the reduction of particle size to simulate worst case scenarios. This practice defeats the whole idea of solidification (solidification in a true sense as opposed to stabilisation) if immobilisation is achieved primarily through physical containment of waste material within the binder matrix (micro-encapsulation).

Another area that is affected by uncertainty is the evaluation of changes in the stabilised waste induced by long-term exposure to various environmental conditions, as well as the implications of these changes with regard to the chemical and structural integrity of the stabilised/solidified waste forms. This uncertainty is amplified by the difficulty in designing the control experiment as far as organic waste stabilisation is concerned. The replacement of organic waste with water in control experiments is generally practised. Whether this is appropriate or not is a matter of debate.

This study aims to outline the effects of mixing ratios in the stabilisation of organic oily sludges using ash-based Solidification/Stabilisation S/S systems. The chemical interaction between synthiol gunk, an organic sludge, and the binder (fly ash and fly ash-slaked lime mixture) is also discussed with some emphasis on the effect of the organic sludge on the mobility of trace elements from the binder. This study is supplemented by a micro-structural analysis of the stabilised products under scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM-EDS).

A comparison of two leaching media with regard to trace elements mobility was conducted

using distilled water (DIN 418 standard leach test) and acetic acid solution (TCLP standard leach test). An attempt to identify elements of concern based on their mobility in the two leaching media was made using calculations based on the estimated environmental concentration (EEC) and acceptable risk levels of trace elements. This was coupled with the discussion of the relevance of legal requirements, as described by the Minimum Requirements document (Department of Water Affairs and Forestry, 1998), on the evaluation of cement-based S/S processes. A short study was also conducted on the effects of synthol gunk, as well as its stabilised derivative, on biomass production of sweetcorn maize. The aim was to determine the threshold loading rate of the waste material leading to visible deterioration in biomass production.

CHAPTER TWO

2. CHEMICAL FIXATION OF HAZARDOUS ORGANIC WASTES USING FLY ASH AND OTHER ADDITIVES: *A LITERATURE REVIEW*

2.1 Introduction

The field of chemical fixation and solidification, CFS in short (also known as Solidification/Stabilisation or S/S), is maturing into an accepted environmental technology. However, few people working in waste treatment have any knowledge of the CFS technology other than that gained from CFS vendors or from superficial reviews in government publications or industry conferences. Furthermore, vendors offering waste treatment and disposal services are not inclined to provide information about the mechanisms whereby their processes accomplish S/S. Even chemical components are kept secret. In many cases the vendors also don't know exactly how their processes work. Despite this lack of fundamental information, in 1992 the S/S technology was chosen by the US EPA as the treatment of choice for 26% of the remedial actions completed at Superfund sites.

The CFS processes are generally designed and used to accomplish one or more of the following objectives: to reduce contaminant mobility and/or solubility, to improve the handling and physical characteristics of the waste by producing a solid with no free liquid and to decrease the exposed surface area across which transfer or loss of contaminant may occur.

The CFS technology involves the use of a suitable binder, which can be inorganic (e.g. hydraulic cement or fly ash) or organic (e.g. asphalt), to chemically and/or physically stabilise hazardous wastes in such a way that they are considered non-hazardous by relevant regulations.

The waste can be solid or liquid and inorganic or organic. This technology has, however, found more applications in hazardous inorganic waste as opposed to hazardous organic waste disposal.

The increases in environmental awareness worldwide as well as advances in environmental legislation have prompted waste generators to consider the treatment of hazardous waste prior to final disposal. With this new approach come treatment costs and efforts for their minimisation. It is for these reasons that CFS is becoming the treatment of choice for a wide variety of hazardous wastes due to its cost effectiveness when compared to other techniques such as crystallisation and incineration.

Although CFS is a promising technology, improvements have proven difficult due to the lack of fundamental information about the mode of action leading to S/S of hazardous waste, especially for organic waste.

In one of the US EPA's technical resource documents (US EPA, 1993), a recommendation was made for the development of methods to determine whether bonding occurs between binder and organic waste. Furthermore, the US EPA mention that increased understanding of the mechanisms for organic immobilisation will speed development of better binders for organic contaminants.

2.2 Mineralogy, Physical and Chemical Properties of Fly Ash

The chemical and mineralogical properties of fly ash depend on the characteristics and composition of the coal burnt at the power plant. Fly ashes are composed chiefly (50 to 90%) of mineral matter in the form of glassy particles (Wesche, 1991). A small amount of ash occurs in the form of crystals. The glass is typical silica-alumina glass and the crystalline components consist mainly of mullite ($3Al_2O_3 \cdot 2SiO_2$), in amounts varying between 6.5% and 34%, and quartz. Small percentages of hematite and magnetite (CUR report, 1992), as well as metallic iron (Willis and Bosch, 1988) have been reported.

Willis and Bosch (1988) also mention the presence of rutile needles and Mn rich magnesioferrite, in fly ash. Helmuth (1987) emphasises the diversity of the chemical composition of fly ashes and mentions a few factors responsible for this diversity. The most important factors are the coal from which the fly ash is derived, the operational conditions of the blast furnace, the particle size of fly ash and additives used to improve the performance of precipitators. Nevertheless, he does stress that glass is the most abundant constituent in fly ashes. Amounts of mineral phases are rather small and do not appear to be directly related to the pozzolanic properties of ashes, except by their influence on the composition of the glass phase. The major crystalline phases in fly ash are quartz, mullite, hematite and magnetite and are neither hydraulic nor pozzolanic.

2.3 Hydration and Pozzolanic Reactions

The first comprehensive study on the use of fly ash as a pozzolan in concrete was described by Davis *et al.* (1937). The use of fly ash in the cement industry is primarily due to its pozzolanic and cementitious properties. According to a definition by the ASTM (1993), a pozzolan is a

siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

High-calcium fly ash (type C fly ash) is capable of independent setting when mixed with water. The hydraulic minerals usually present in high Ca fly ash react in a manner entirely analogous to their reaction in portland cement (Wesche, 1991). The four main reactive hydraulic minerals are tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$) and tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$ also known as hydrogarnet).

These minerals undergo hydration according to the following main reactions:

$$2Ca_3SiO_5 + 6H_2O = Ca_3Si_2O_7{\cdot}3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2Ca_2SiO_4 + 4H_2O = Ca_3Si_2O_7{\cdot}3H_2O + Ca(OH)_2 \quad (2)$$

$$Ca_3Al_2O_6 + 3CaSO_4{\cdot}2H_2O + 26H_2O = Ca_6Al_2O_6(SO_4)_3{\cdot}32H_2O \text{ (ettringite)} \quad (3)$$

$$Ca_3Al_2O_6 + CaSO_4{\cdot}2H_2O + 10H_2O = Ca_4Al_2O_6SO_4{\cdot}12H_2O \text{ (monosulfoaluminate)} \quad (4)$$

$$Ca_3Al_2O_6 + Ca(OH)_2 + 18H_2O = Ca_4Al_2O_7{\cdot}19H_2O \text{ (tetracalcium aluminate)} \quad (5)$$

$$Ca_4Al_2O_7Fe_2O_3 + 2Ca(OH)_2 + 10H_2O = Ca_6Al_2Fe_2O_{12}{\cdot}12H_2O \text{ (tetracalcium aluminoferrite)} \quad (6)$$

In cement chemistry, symbols such as C-S-H for calcium silicate hydrate, A*fm* for the monosulfoaluminate and A*ft* for the trisulfoaluminate (ettringite) are constantly used since the stoichiometric representation denoted in reactions 1 to 6 is somewhat misleading because the actual compositions of the hydrates are indefinite (Helmuth, 1987). In fact, Copeland *et al.* (1967) showed that the calcium silicate hydrates react with aluminates, ferrites, and sulfates to form substituted calcium silicate hydrate gels containing small amounts off the oxides of

aluminium, iron and sulfur and that the C-S-H in cement pastes was likely to have a higher Ca to Si ratio than that of tricalcium silicate pastes.

Reactions 1 and 2 provide calcium hydroxide required by pozzolanic reactions while reactions 5 and 6 consume $Ca(OH)_2$ and hence form a competition with pozzolan in fly ash.

The pozzolanic reaction starts when the glass of the fly ash particles dissolves, a process which appears to be strongly dependent on the alkalinity of the pore water (CUR, 1992). Wesche (1992), agrees that the glass phase of fly ash is affected by pozzolanic activity, noting that this activity is evident from 14 days onwards and that after 120 days the fly ash particles are practically disintegrated as a result of attack by $Ca(OH)_2$ produced by the hydration reactions 1 and 2.

An important parameter in cement chemistry is the pozzolanic activity index, described by Soerensen (1981) as the weight of cement that can be replaced by one unit weight of fly ash (or pulverised fuel ash) without altering the concrete compressive strength at a given age.

The pozzolanic activity index with portland cement is:

$$\text{Pozzolanic activity index} = \left(\frac{A}{B}\right) \times 100$$

where A and B are the average compressive strength of the test mix cubes and control mix cubes, respectively. Generally, the finer the fly ash and the lower the carbon content, the greater will be the pozzolanic activity and the greater the contribution to strength in concrete of the same workability at a given age (Frohnsdorff and Clifton, 1981). The apparent interruption of pozzolanic reactions by organic carbon has serious implications for the CFS of organic contaminants using fly ash.

2.4 Solidification/Stabilisation

2.4.1 Definition

The US EPA defines solidification and stabilisation as follows:

Solidification refers to the techniques that encapsulate the waste in a monolithic solid of high structural integrity. The encapsulation may be of fine waste particles (micro-encapsulation) or of a large block or container of waste (macro-encapsulation). Solidification does not

necessarily involve chemical interaction between the waste and the solidifying reagents, but may mechanically bind the waste into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the waste within an impervious capsule (Cullinane and Jones, 1986).

Stabilisation refers to those techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilisation. A much simpler definition of these two terms provided in a very useful US EPA technical document (US EPA, 1993) is as follows:

Solidification refers to a process in which materials are added to the waste to produce a solid. This may or may not involve chemical bonding between the toxic contaminant and the additive.

Stabilisation refers to converting a waste to a more chemically stable form. This conversion may include solidification, but it almost always includes use of a physicochemical reaction to transform the contaminant to a less mobile or less toxic form. Biological processes are not included in this definition. The term monolith is a misnomer as it implies that the final product is a block of stone, which does not fit many of the processes in use today that produce a soil-like solid. Conner (1990) prefers to use the terms fixation, chemical fixation and stabilisation interchangeably because of the disagreement among researchers in the field about the use of the terms solidification and stabilisation.

2.4.2 General

More is known about metal fixation than about fixation, destruction and immobilisation of any other hazardous constituent group encountered in CFS technology (Conner, 1990). This is because metals are the only really hazardous constituents that cannot be destroyed by thermal or chemical methods. The discussion in this review will focus more on the fixation of organic and/or organic-containing wastes.

There are five distinct types of organic-containing wastes that might be encountered in CFS treatment (Conner, 1990):

- Oil-based and solvent-based wastes such as solvent, distillation bottoms and refinery wastes.

- Aqueous wastes containing 1 to 20% or more of soluble or insoluble, emulsified organics that are considered hazardous by the RCRA (Resource Conservation and Recovery Act) in the U.S.

- Aqueous wastes containing 1 to 20% or more of soluble or insoluble, emulsified organics that are considered non-hazardous by the RCRA (Resource Conservation and Recovery Act) in the U.S

- Aqueous wastes containing small amounts (10 to 1000 ppm) of hazardous organic contaminants.

- Aqueous wastes containing less that 1% (usually 10 to 100 ppm) of non-hazardous organic contaminants of interest in CFS only when they affect cementitious and other reactions of the CFS system.

Aqueous waste streams containing small amounts (10 to 1000 ppm) of hazardous organic contaminants are the most treatable organic waste forms under S/S technology (Conner, 1990). Containment will be most effective for most immiscible liquids and least effective for water soluble liquids using normal cement-based methods (Conner, 1990). It is unclear, however, whether appreciable chemical reactions take place in the matrix. Losses may be caused by other factors such as volatilisation in S/S processes involving high temperatures (Weitzman *et al.*, 1987).

Hazardous organic contaminants can be separated into two categories, those that have high water solubility and those that have very low water solubility. Although the problems associated with the CFS of water soluble organic contaminants are not properly understood at a fundamental level, there are possibilities that have been suggested by Conner (1990). These are discussed in section 2.4.5.

Leaching tests, such as the Toxicity Characteristic Leaching Procedure (TCLP), are used to assess the success of CFS applications and are generally water based, hence immiscible organics become less of a problem except for other properties such as volatility and flammability.

Water-soluble organics tend to be more polar and may interact with cations to form soluble complexes. Of major importance is the capacity of organic ligands, such as gluconate, EDTA,

glycine and nitrilotriacetate, to form chelates with metal ions.

When a ligand forms a water-soluble chelate complex, it is called a sequestering agent. In this form, the metallic ion is inactivated and no longer participates in its usual chemical reactions, but it will be readily leached out by leaching tests. Ligands may, therefore, interfere with CFS processes by sequestering ions that participate in CFS reactions, such as aluminium.

Normal environmental conditions are not oxidising enough to destroy chelating complexes, necessitating the deliberate addition of strong oxidising agents such as $KMnO_4$ and H_2O_2. While these may destroy the contaminant of interest, they may create a hazardous species from other organics in the waste which were previously non-hazardous. The presence of chromium may also pose the risk of the formation of Cr^{6+}, necessitating a subsequent reduction step.

2.4.3 Binders

There are inorganic and organic binders that can be used to stabilise various hazardous wastes. Cement based and pozzolanic processes are the methods of choice in the CFS industry, probably because of their low cost. The most common inorganic binders are:

- Portland cement
- Lime/fly ash
- Kiln dust (lime and cement)
- Portland cement/fly ash
- Portland cement/lime
- Portland cement/sodium silicate

The versatility and adaptability of cement-based solidification and stabilisation processes was noted by the US EPA (1986c), as well as the possibility to form waste/cement composites that have good strength and durability. One of the disadvantages with cement-based systems is porosity. However, sorbents and/or emulsifiers can be added to reduce contaminant migration through the porous solid matrix.

Pozzolans contain significant amounts of silicates, which distinguish them from lime-based materials. The primary containment mechanism for pozzolans such as fly ash, pumice and lime kiln dust is precipitation and physical immobilisation. The U.S EPA (1986c) reported that the

addition of bentonite can substantially reduce the amount of fly ash required. Typically, pozzolanic reactions occur more slowly than do cement reactions (US EPA, 1993). According to the US EPA (1986c) some type C fly ashes have enough lime to be not only pozzolanic but also self cementing. In general, lime/fly ash-solidified wastes are not considered as durable as Portland cement-treated wastes.

Parsa *et al.* (1996) reported on the use of type C fly ash as the only binder in the S/S of a liquid waste stream containing nitrates of Cr, Cd, Al, Mg, Fe, K, Na as well as nitric acid. They claim to achieve this by adjusting the pH to an optimum of 9.2 and compacting the waste for 3 seconds at 4.65MPa after less than 30 seconds of mixing. These results were assessed with the TCLP.

Ettringite ($Ca_6Al_2O_6(SO_4)_3 \cdot 32H_2O$) is a very expansive salt due to its high content of water of hydration. If ettringite crystallises while the S/S-treated waste is still plastic, it can be accommodated in the structure and contribute to the final strength. However, if the ettringite forms after the grout has become rigid, it can undermine the structure by forming cracks as it expands.

Organic binders, which are commercially employed for the solidification of hazardous organics and radioactive waste, are not as frequently used as inorganic binders due to costs and difficulty of application. The following organic binders have been tested or used for S/S:

- Asphalt (bitumen)
- Polyethylene
- Polyesters
- Polybutadiene
- Epoxide
- Urea formaldehyde
- Acrylamide gel
- Polyolefin encapsulations

Organic binders will not be discussed in detail in this review. Many organic binders require heating (thermoplastic and thermosetting processes) as an initial step. This is followed by controlled cooling; hence they require more specialised equipment than inorganic binders.

Some of a few problems with organic binders are:

- Many are hydrophobic and are therefore not compatible with water-based wastes
- Biological action and exposure to ultraviolet light may induce degradation. Long term stability becomes a critical factor.
- Some solvents and greases can prevent hardening of binders such as asphalt.

2.4.4 Additives

Cement and pozzolan processes produce porous, solid products and it may be necessary to add certain reagents to immobilise specific contaminants or to improve the immobilisation process and mitigate the effects of certain inhibitors.

Some previously used additives and their applications are as follows (US EPA, 1993):

- *Soluble silicates* to reduce interference of metal ions and to "flash set" cement to produce a low strength concrete.
- *Selected clays* such as bentonite can reduce the amount of sorbent required in low-solids mixtures.
- *Surfactants and emulsifiers* for mixing non-polar organic liquids such as waste turbine oil and grease into cement blends.
- *Carbon, cellulosic and zeolitic material* for retainment of toxic constituents.
- *Activated carbon* as sorbent for organics.
- *Lime, soda ash, caustic soda, and magnesium hydroxide* for maintaining alkaline conditions.
- Reducing agents, organophilic clays and organosilanes.

Other additives are still being researched further. Lange *et al.* (1996) found that curing solidified waste under an atmosphere of carbon dioxide increases the calcite content of the solid while decreasing the concentration of C-S-H. These changes, induced by carbonation, were found to be beneficial. It would be interesting to determine the effects of compacting fly ash-treated waste under a carbon dioxide atmosphere.

2.4.5 Reaction Principles In Organic Chemical Fixation and Stabilisation (CFS) Systems

Aside from adsorption, volatilisation and biodegradation (which is practically insignificant due to the high alkalinity associated with the CFS system), the most likely reactions fall into four categories. Hydrolysis, oxidation, reduction and salt formation. Table 2-1 shows some typical conversions that are possible in the CFS of organic material.

Table 2-1: Some possible organic reactions in the CFS system (Conner, 1990)

Reactants	*Products*
Hydrolysis	
Alkyl halides + H_2O	Alcohols + Inorganic acids (halides)
Organic amines	organics + ammonia
Oxidation	
Phenol + $14H_2O_2 + Fe^{2+}$	$6CO_2 + 17H_2O$
$R–CH_3$	R–COOH
$R–CH_2OH$	R–COOH
RCHOH–CHOR	R–COOH + R–COOH
R–CHO	R–COOH
R_2CH_2	R_2CO
$R_2CH(OH)$	R_2CO
R_3CH	$R_3C(OH)$
R_3CH + HCR	$R_3–C–C–R_3$
$R_2N–H + H–NR_2$	$R_2N–NR_2$
RCH=CHR	RCHOH–CHOHR
2R–SH	R–S–S–R
R–S–S–R	$RSO_3H + RSO_3H$
Reduction	
$Fe + 2H_2O + 2RCl$	$2ROH + Fe^{2+} + 2Cl^- + H_2$
Salt formation	
Oxalic acid	Calcium oxalate

"R" denotes the remainder of the organic molecule

Hydrolysis usually results in the exchange of the hydroxyl group (–OH) for another functional group. According to Dragun (1988), the rate law for hydrolysis is expressed as:

$$K_L = \left(\frac{K_B \cdot K_W}{[H^+]}\right) + K_A \cdot [H^+] + K_N \qquad (7)$$

Where K_A, K_B and K_N are the second order rate constants for acid, base and neutral processes, respectively, and K_L is the pseudo-first order rate constant observed for the hydrolysis at a specific pH and temperature.

Equation 7 shows the role of pH on hydrolysis with respect to which rate constant is dominant at a given pH.

Oxidation of organics occurs via two pathways (Dragun, 1988). One is the heterolytic pathway in which the electrophilic attack removes an electron pair. The other is a homolytic pathway in which only one electron is removed, resulting in radical formation. According to Conner (1990), oxidation and hydrolysis are probably the most common reactions for organics in CFS systems.

Reductive alteration of organic contaminants in waste is probably the least studied and the least understood subject. In organic terms, reduction means an increase in the hydrogen content or a decrease in the oxygen content of an organic compound. Reduction may become important when the final solidification product is considered on a long term basis once all the oxidants have been used up.

Salt formation is another area of CFS of organics that has not been well documented. When working with ethylene glycol and *p*-bromophenol, Chou *et al.* (1988) observed changes in morphology and electron diffraction patterns in cement matrices which they could not correlate with any of the expected products of hydration. This may be attributable to salt formation. Chemistry shows that some organic compounds (especially organic acids) can crystallise into insoluble salts. Conner (1990) noted this as a fertile area for research in the immobilisation of trace organics.

2.4.6 Solidification/Stabilisation Of Organic Wastes

Destructive processes such as incineration, biodegradation, chemical oxidation and dechlorination have always been treatments of choice for wastes with very high concentrations of hazardous organic compounds. Organic contaminants are more difficult to treat with inorganic CFS processes than are inorganics such as metals and metal compounds. The main

challenge is that they are nonpolar and hydrophobic, whereas inorganic CFS binders are polar and hydrophilic. Organic contaminants do not normally react with an inorganic matrix but instead are sorbed or encapsulated within pores. Additives are sometimes added to increase the binding affinity for organic contaminants.

Given in Table 2-2 are some solidification/stabilisation processes that have been successfully applied at least once in the treatment of the indicated contaminant. Important issues that were not addressed in these treatments are the degree of stabilisation, long-term stability and volatilisation (as opposed to immobilisation) (US EPA, 1993).

Table 2-2: S/S processes tested on or applied to organic-containing wastes (US EPA, 1993)

Binder	*Organic Contaminant*	*Physical Form of Waste*	*Reference*
Bitumen	Oil and Gasoline	Soil	US EPA (1989g)
Chemfix*	Oil	Sludge	
Kiln dust	Oil	Sludge	
Kiln dust	Creosote	Sludge	
Lime and fly ash	Organics	Sludge	
Lime and kiln dust	PCBs and dioxins	Sludge	
Portland cement, kiln dust, and a proprietary agent	Pesticides	Sludge	
Portland cement and polymer	Kepone	Soil	
Portland cement and a proprietary agent	Oil	Sludge	
	Vinyl chloride and ethylene chloride	Sludge	
	API separator sludge	Sludge	
	PCBs	Soil	
Pozzolan and proprietary agent	Oil	Soil	
Fly ash	Phenol	Sludge	Côté and Hamilton (1984)
Lime and Fly ash	Phenol	Sludge	
Portland cement	Phenol	Sludge	
Portland cement and clay	Phenol	Sludge	
Portland cement and fly ash	Phenol	Sludge	
Portland cement and soluble silicate	Phenol	Sludge	
Organic	Kepone	Sediment	Conner (1990)
Portland cement	Latex	Waste caulk	

Portland cement and soluble silicate	Kepone	Sediment	
Sulfur-based	Kepone	Sediment	
Lime and nucleophilic reagents	PCB	Soil	HazTech News (1991)
Portland cement and clays	Substituted phenol	Solution	Sheriff *et al.* (1989)

* chemfix is a proprietary agent.

The interaction between the organic contaminant and the binder is not well understood and it has been difficult to determine whether the apparent decreased contaminant mobility is caused by sorption effects, dilution by reagent additions, sample heterogeneity or volatilisation.

One of the potential pitfalls of using S/S technology to treat waste with significant nonpolar organic contaminants is the inability to adequately assess the extent of contaminant immobilisation attributable to S/S treatment (US EPA, 1993).

Another potential problem for consideration arises due to the aggressive chemical environments associated with S/S inorganic binders, such as increased temperatures and alkaline pH. These may lead to degradation and transformation of some organic compounds. This may erroneously be interpreted as stabilisation of a particular contaminant, where in fact the contaminant has merely been transformed to other products, which may or may not be hazardous. The cost of identifying and characterising the toxicities of by-products (or fumes in the case of volatile organics) may be inhibitory.

2.4.7 Performance Assessment

A number of tests can be performed on treated waste to assess the effectiveness of the treatment. The tests are chosen according to, or to satisfy, the data quality objectives. Perhaps the most useful tests are the strength tests, the leaching tests, flammability tests (especially in the treatment of organics) and durability.

The Unconfined Compressive Strength (UCS) test is the most popular in the cement chemistry. But, if the final disposal site for the treated waste is expected to be saturated with water (either from a fluctuating water table or heavy rainfalls), it may be necessary to conduct the Immersion Compressive Strength test, where the sample is soaked in water prior to compressive loading.

The TCLP is recognised as the leaching test of choice in South Africa as defined by the

Department of Water Affairs and Forestry in their publication of the 2nd edition of the Minimum Requirements document (DWAF, 1998).

No standards have been produced to determine acceptance after durability testing, partly because calibration relative to real disposal environments has not yet been achieved (US EPA, 1993). The durability test is therefore only useful for comparing one CFS process with another.

2.5 Conclusions

Although CFS is more adapted to hazardous inorganic wastes, some effort is being shown by scientists to incorporate the treatment of hazardous organic waste by this technique. It is, however, noted that the treatments of choice for hazardous organic waste are destructive thermal and biological processes. CFS should be considered if these are either unsuitable or cost intensive.

Problems associated with the treatment of hazardous organic waste by CFS using inorganic binders include hydrophobicity of organic waste, volatility, chelation by water soluble organic compounds and chemical transformations of organic compounds.

Organic binders are being developed but the success of their development is hindered by the lack of knowledge about the mechanisms involved in the stabilisation processes.

Potential areas of research include the determination of whether stabilisation, as opposed to physical immobilisation, occurs between inorganic binder and organic waste and to what extent. Determination of the effect of the type of organic compound on the S/S process will facilitate the development of more effective pre-treatment steps to remove/transform specific compounds known to interfere with the S/S process. The identification of additives to improve the stabilisation process is another important area of research as well as salt formation, especially if the additive is a strong oxidising agent that may lead to the formation of organic acids.

CHAPTER THREE

3. CHARACTERISATION OF ASH AND PREPARATION OF STABILISED WASTE FORMULATIONS

3.1 Introduction

Stabilisation/solidification of hazardous waste involves mixing the waste material with a binder, which in this study is ash and/or lime. Due to the diversity of waste materials, the appropriate ratio of waste to binder becomes a highly variable factor. This necessitates optimisation of the mixing ratio between binder and waste for best results, which could not be done in this study due to time constrains. What was done instead was to ensure the saturation of the waste material (the petrochemical synthiol sludge) with the binder. This ensures that there is no competition for available binding surface on binder particles between waste constituents.

It is well known that fly ashes from different coal types and from different process operating conditions differ in their chemistry as well as their composition (see section 2.2). It is therefore essential to characterise the ash that was utilised for the study. Characterisation is even more important in this study because the ash that was used cannot be considered "clean" in that it has been transported within a recycled effluent into which other waste streams have been introduced.

The aim of this chapter is to provide an understanding of the procedures followed in preparing stabilised waste formulations as well as describing the nature and state of the ash that was used as a binder. This chapter also provides a critical analysis on the choice of the binder system as well as suggestions on how the stabilised waste forms can be improved.

3.2 Sampling and analytical methods

3.2.1 Sampling

The ash used in this study originates from a coal power station operated by Sasol, a South African company that produces hydrocarbon fuel and chemicals from coal. The ash is transported to the ash slimes dams as a slurry of 1 part solids (which are primarily ash) to 5 parts aqueous phase. The aqueous phase is composed of recycled clear ash effluent (CAE) to which a

number of other aqueous waste streams have been introduced.

At the slimes dams, the ash is allowed to settle while the aqueous phase drains out and is recycled. In this process, the ash acts as a micro-filter, which adsorbs and traps inorganic salts from the aqueous phase. The ash samples were collected from these slimes dams in a slightly damp state and were air-dried before analysis.

The synthol sludge, also obtained from Sasol, was received in metal cans and no details of sampling procedures were available.

3.2.2 Characterisation of ash

3.2.2.1 Physical characterisation

The particle size analysis was performed on the Ash sample using a laser diffraction size analysis technique. This was done using the Malvern Mastersizer Particle Size Analyser. Sonication of the samples was not done, only the pump and the stirrer, both set at 70%, were used together with a wide range 1000 mm lens.

In the laser diffraction technique, monochromatic light is passed through a dilute suspension of fly ash in water. The angular distribution of diffracted light is detected and quantified. The angle of diffraction increases with decreasing particle size. The sample and instrumental settings are given in Appendix 7.1.

3.2.2.2 Mineralogical characterisation

XRD analysis was performed on Ash and the lime-ash mixture (LASH). Each sample was ground into a powder in an agate crucible. The powder sample was placed in an aluminium plate and flattened. The plate was mounted into the Philips PW 1390 X-ray diffractometer equipped with a Cu Kα X-ray tube. Peaks were analysed and identified using the X'Pert Data Collector software version 1.1b. Sample and instrumental settings are given in Appendix 7.1.

3.2.2.3 Elemental characterisation

The analysis of major elements was done on fusion discs using a wavelength dispersive Philips

PW X'Unique II X-ray spectrometer. Approximately 3g of sample were dried at 105°C overnight to determine residual water content. The sample was then baked at 800 °C in a furnace for 4 days to determine the loss on ignition (LOI). The samples were allowed to cool to room temperature. Fusion discs were made by combining 0.7g of baked sample with 6 g of Sigma 12:22 flux and 4 drops of a wetting agent (2.9*M* LiBr.). The discs were produced using a Claisse Fluxy instrument and were kept in a desiccator until the time of analysis. Instrumental settings and calibration are given by Willis (1995).

3.2.3 Preparation of stabilised waste formulations

3.2.3.1 Slaked lime-ash mixture (LASH)

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (450 g) was mixed with laboratory grade $Ca(OH)_2$ (50 g). Distilled water (232 ml) was added to the mixture to achieve a saturated paste, which was left to cure to near dryness. The slightly soft monolithic solid obtained was manually crushed to a powder, which was subsequently sieved through a 2 mm sieve.

3.2.3.2 Synthol gunk-ash mixture (GASH)

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (425 g) was added to synthol gunk (75 g) in a 1L plastic container in small quantities with frequent mixing to achieve good mixing of the two waste materials. This resulted in a soil-like black powder with grey specks of fly ash.

Two batches of GASH were prepared with the one described above being prepared for use in leaching experiments. A second batch of GASH was prepared for use in plant growth experiments. This sample of GASH was prepared by adding Ash (1000 g) to synthol gunk (200 g) in small quantities with frequent mixing to achieve good mixing of the two waste materials. A soil-like black powder was obtained to which distilled water (375 ml) was added to form a workable mixture in the form of a paste. The paste was left to "cure" until it was dry enough to be filtered through a 2 mm sieve. The addition of water resulted in a more uniform mixture of synthol gunk and ash with no grey specks of ash in the sample.

3.2.3.3 Synthol gunk-slaked lime-ash mixture (GLASH)

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (382.5 g) was mixed thoroughly with laboratory grade $Ca(OH)_2$ (42.5 g). The resulting mixture was added to synthol gunk (75 g) in a 1L plastic container in small quantities with frequent mixing to achieve good mixing of the two waste materials. This resulted in a soil-like black powder with grey specks of fly ash.

3.2.3.4 Pellet preparation

Pellets were prepared from the stabilised waste formulations (LASH, GASH and GLASH) by weighing out 10 g of the stabilised material and pressing at a pressure of 2 tons on ram for 2 minutes. Each pellet had the following approximate dimensions:

- Radius 15.5 mm
- Height ± 8 mm
- Mass 10 g
- Density 1.677 g/cm^3

3.3 Results

The particle size analysis of Ash, presented in Figure 3-1, shows a two-mode distribution of particles. A larger fraction of particles has a particle diameter of between 140 and 164 μm, a smaller size fraction is between 9 and 10.5 μm with the average particle size of 116.7 μm. Particle size analysis results gave an estimate of the specific surface area of the Ash sample that was found to be 0.0494 m^2/g.

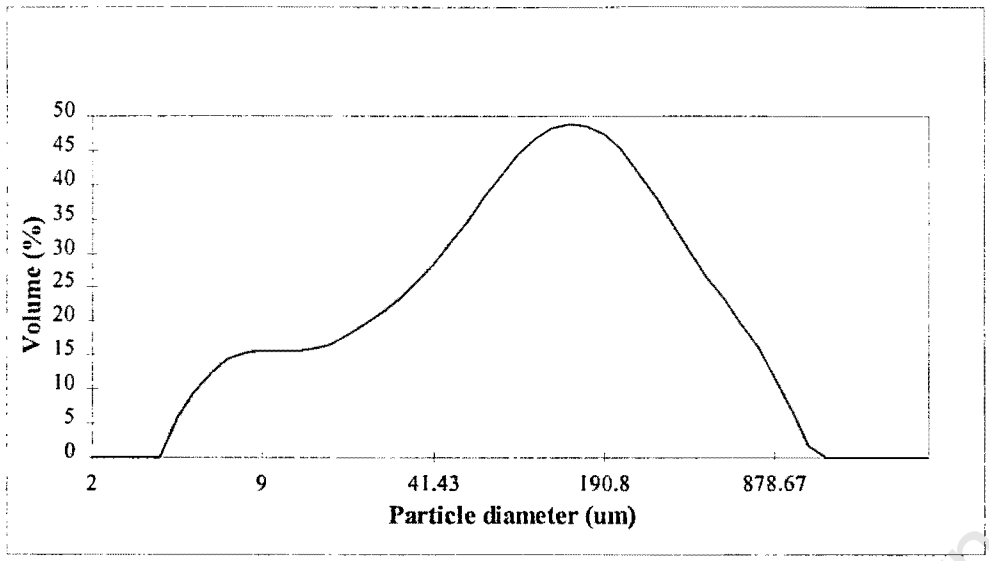


Figure 3-1: Particle size distribution of Ash shows a bi-modal distribution

The XRD pattern of Ash presented in Figure 3-2 shows the major crystalline phases present in the original sample of Ash. These were found to be Quartz (Q), Mullite (M) and Calcite (C) The d-spacing data of both patterns (Figure 3-2 and Figure 3-3) are given in Appendix 7.

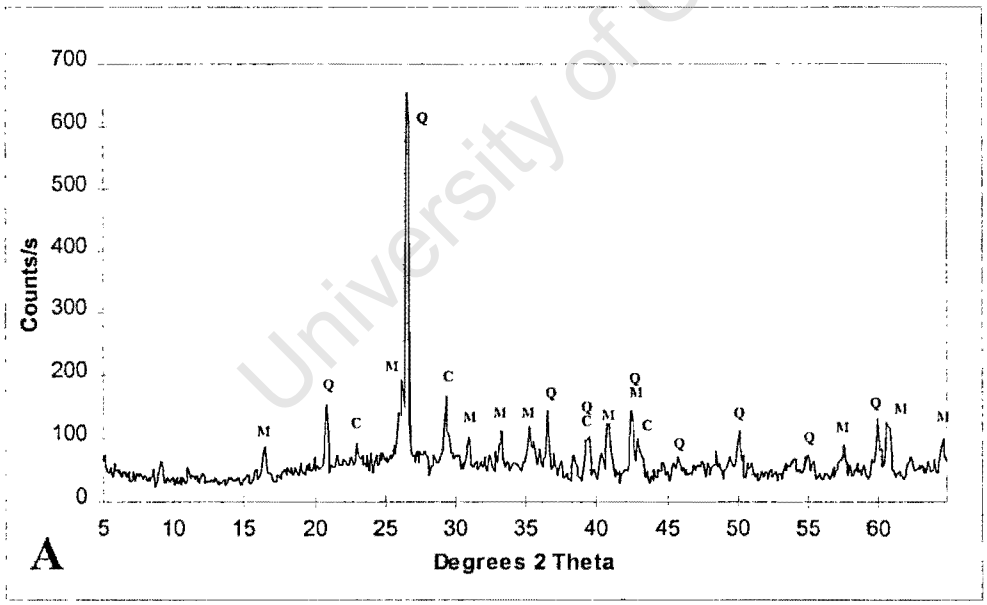


Figure 3-2: An XRD pattern of Ash showing Mullite (M), Quartz (Q) and Calcite (C) peaks

The only major difference between Ash and LASH is the presence of portlandite in LASH as

shown in Figure 3-3. The calcite peaks appear to have a higher intensity on LASH, with more intense peaks between 45 and 50°2θ, and at 55°2θ and 28°2θ. This high intensity may be due to the orientation of the phases in the plate, but it could also suggest higher calcite contents in LASH due to higher slaked lime contents and exposure to atmospheric CO_2.

This peak intensity difference is evident even when the difference in scales of counts/s is taken into account. While calcite peaks become more intense, mullite peaks appear to weaken on LASH than on Ash.

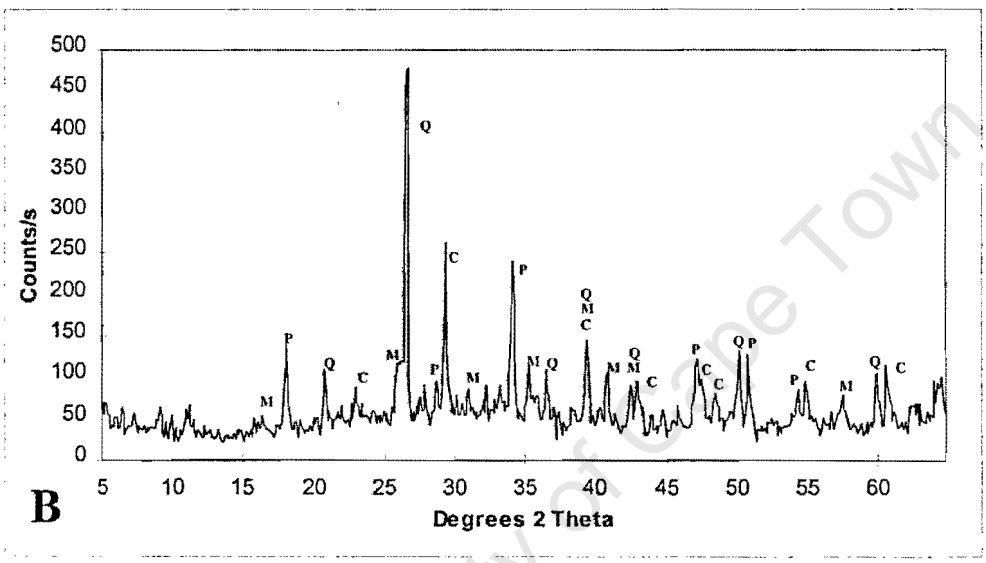


Figure 3-3: XRD pattern of LASH showing Mullite (M), Quartz (Q), Calcite (C) and portlandite (P) peaks.

The analysis of major elements by wavelength dispersive XRF shows Si to be the dominant element in Ash, followed by Al, which is typical of fly ash. A comparison of Ash and LASH shows that most elements assume a concentration decrease in a manner that is consistent with the addition of slaked lime in LASH. A decrease in Cr is somewhat pronounced, probably due to the lower Cr concentrations causing large variations in analytical results caused by a small biased error.

It is not understood why Na and Ni appear to be unaffected by the introduction of slaked lime in the Ash. The higher water content in LASH could be due to the fact that water was added to LASH during curing and may not have been completely utilised or evaporated at the time of

analysis. The LOI also appears to be higher in LASH corresponding to the expected higher calcite content in LASH in which the carbonate would contribute to the LOI.

The higher calcium content in Ash compared to LASH could be due to the high LOI and H_2O in LASH compared to Ash. The high water in LASH is a result of a hydration dilution effect due to the addition of slaked lime. The Ca/Si ratio for Ash and LASH is the same at 0.3.

Table 3-1: Major elements in the solid Ash and LASH samples analysed by WDXRF. The data have been reworked from oxides to elements.

Element (Wt %)	*Ash*	*LASH*	*% drop**
Si	21.872	19.173	12.3
Ti	0.754	0.650	13.8
Al	11.552	10.075	12.8
Fe	3.316	3.067	7.5
Mn	0.054	0.045	16.7
Mg	1.705	1.480	13.2
Ca	7.137	6.194	13.2
Na	0.304	0.304	0.0
K	0.661	0.577	12.7
P	0.316	0.277	12.3
S	0.239	0.217	9.2
Ni	0.005	0.005	0.0
Cr	0.014	0.011	21.4
H_2O	2.88	11.74	
LOI	5.42	7.35	
Total	98.352	98.086	

*** % drop is the percent decrease in the concentration of elements from Ash to LASH. Ideally this decrease should correspond to 10% slaked lime added in LASH.**

3.4 Discussion

3.4.1 Characterisation of ash

3.4.1.1 Particle size

The average particle diameter of fine ash (116.69 μm) was found to be more than double the value of 50 μm reported by Helmuth (1987). This explains why the Sasol ash has a low CaO content since the finer fraction of fly ash are richer in CaO, while calcium in the larger particles is mostly present as part of the glass phase and is not readily available for reaction.

A study conducted by Campbell (1999) on unweathered Sasol fly ash showed a three-mode particle size distribution pattern. The smaller size was found to be between 0.31 and 0.36 μm while the largest mode was made up of particles with 121 μm diameter. The third mode, which was not commented on, was a shoulder of the largest mode with a particle size diameter slightly larger than 10 μm.

The smallest mode and the shoulder mode seem to have disappeared in the weathered fly ash, with an appearance of a new mode at 9-10 μm. There are four possible events that can lead to this. The first is the natural variation of fly ash composition caused by a number of factors including the varying nature of the parent coal as well as furnace operating conditions. The second event would be the agglomeration of the smallest mode through hydration reactions and/or adsorption of dissolved matter from the transport solution resulting in the increased particle size observed in weathered fly ash. The third event would be the weathering of the shoulder mode by the transport solution, with a possible interaction of solution constituents to catalyse the weathering process, resulting in a decreased particle size. Lastly, it was mentioned that sonication of samples was not performed. Campbell (1999) treated his sample with ultrasound and this appears to be a strong possible cause of the variation between the two sets of results.

The observed shift of the largest mode towards larger particle size (from 121 μm to 141-164 μm) could be the result of adsorption of contaminants from the transport solution and/or hydration reactions.

3.4.1.2 Major elements

The XRF analysis given in Table 3-1 suggests that the ash has a significant Al content. XRD data on Figure 3-3 A indicates that some of the Al is present as mullite, which is not readily available for reaction processes within the pozzolanic system. Mullite may, however, be involved in adsorption processes. The weaker peak intensity of mullite on LASH may suggest that mullite does weather during hydration, but the weathering could be particularly slow.

A comparison of these results with results from previous studies on unweathered Sasol fly ash (Campbell, 1999) given in Table 3-2, shows that the weathered ash has a low Si content.

Campbell (1999) did notice the decrease in Si with time in Sasol's unweathered fly ash. In the current study it is thought that the low Si content in ash is due to weathering during transport of ash to the ash slimes dams, but variations in the parent coal material may have also played a role. Amounts of Ti and Al were also found to have decreased, probably due to the same reasons mentioned for Si.

Amounts of the rest of the oxides were found to have increased compared to amounts in unweathered ash from the previous study, especially Ca and S. These two elements are thought to bear their high content from the hot lime softening plant effluent, entering the ash system as gypsum. The other elements may also have been adsorbed material from the transport system.

The higher Ca content in the Ash compared to that in the LASH could not be explained and could only be attributed to analytical error.

Table 3-2: Major elements by WDXRF as oxides from Sasol's weathered (current study) and unweathered (after Campbell, 1999) fly ash

Oxide	*Weathered fly ash (%)*	*Unweathered fly ash (%)*
SiO_2	46.79	52.98
TiO_2	1.26	1.69
Al_2O_3	21.83	28.45
Fe_2O_3	4.74	3.33
MnO	0.07	0.042
MgO	2.83	1.35
CaO	9.986	6.40
Na_2O	0.41	0.40
K_2O	0.796	0.46
P_2O_5	0.72	0.255
SO_3	0.597	0.286
LOI	5.42	4.43

The XRD diffractograms presented in Figure 3-3 suggest that the major crystalline phases in both Ash and LASH are quartz, calcite and mullite, with the only difference in LASH being the presence of portlandite, which could most likely be the unreacted $Ca(OH)_2$ originally added to LASH. Contribution from hydration reactions is, however, also possible.

No traces of ettringite could be found in either sample. It is worth mentioning that the XRD patterns were not collected on the finer fractions of the samples; they were in fact collected

on the less than 2 mm fraction that was crushed into powder. Dilution of hydration products by quartz and other crystalline and amorphous material is possible.

3.4.2 The organic sludge

The synthol gunk can be described as filtered residue material from a deactivated iron catalyst from the synthol process. This is a process that converts synthesis gas into a variety of hydrocarbon compounds at Sasol. The filtered material is composed mainly of heavy hydrocarbons and oils. Volatile organic compounds and semi-volatile organic compounds as well as a mixture of oxygenates have been identified as forming part of the synthol sludge (Ginster *et al*, 1999). Forming part of the sludge is the iron catalyst residue as well as other proprietary additives that are introduced in minor quantities to improve the hydrocarbon conversion process.

3.4.3 Mixing of ash and the organic sludge

It has been mentioned that water was not added during mixing of the binder materials and the organic sludge. According to the definition of a pozzolan, water and lime must be added before pozzolanic reactions can take place. The system used in this study can therefore not be described as a pozzolanic system as it does not achieve stabilisation through pozzolanic activity, despite ash being a pozzolan.

The addition of lime in the pozzolan system is generally aimed at reinforcing pozzolanic activity leading to increased strength in the solidification products. The final product in this study was a soil-like powder, which is far from being a solidified monolithic type of end product. This raises some questions about the benefits of adding lime to ash in the stabilisation of organic sludges.

Some researchers working on a proprietary agent referred to as HWT-22 (Newton, 1988), which is a silicate based technology utilising organophilic smectites, which was also being investigated for the stabilisation of waste material with a high organic content, suggested a chemical interaction between silicate layers and substituted aromatic functionalities in the waste. Their observations were based on wavenumber shift between treated and untreated waste material when analysed by FTIR spectrometry.

Fly ash can be expected to behave in a similar manner to these silicate layers in smectites because it is a siliceous-aluminous material. If this was the case, two questions should be considered when using ash that has been or is being used as a salt sink:

1. How does waste already adsorbed on ash particles affect the adsorption properties of ash towards organic material.

2. How does the organic sludge affect the waste material already adsorbed on the ash particles.

3.4.4 Pelletilising

The pellets were prepared to minimise differences in leaching rates due to different porosities of the stabilised products. Pellets would also be convenient to analyse under SEM for differential leaching patterns of stabilised products.

The mixing ratio of 1 sludge to 5.67 ash was chosen for two main reasons. The first was the time constraint which made it impossible to investigate the best mixing ratio of ash to the sludge; hence a decision was made to saturate the sludge with the ash. The second reason was the discovery that oil oozes out of the pellets during pressing at mixing ratios below 1 part sludge to 5.67 parts ash.

The addition of water to the stabilised product was found to enhance homogeneity of the stabilised mixture, signifying improved mixing. But water, just like oil, was found to ooze out during pellet preparation, despite the mixture being left to evaporate for approximately 7 days and the fact that it was sufficiently dry to be handled without sticking. This suggests that water is excluded to a significant degree from interacting with components of the stabilised mixture. Moreover, the evaporation rate is lowered by the presence of an organic film around ash particles which pack together to form a barrier which slows down evaporation. As a result water was only added to the mixture that was used for plant growth experiments.

3.5 Conclusions and recommendations

From this chapter it emerges that the weathered ash used as a binder has been previously used as a "salt sink" and as a result some of its adsorption properties may have been altered and some of its adsorption sites may already be occupied. These sites may be occupied in an

irreversible or reversible manner. In the case of the latter there may be a negative impact on the leachate quality of the stabilised products. This means that results obtained from this study should be treated with care to avoid incorrect generalisation of the behaviour of this particular sample of ash to any other sample of unweathered ash.

It is very important to make a clear distinction between LASH and GLASH. LASH is an ash-lime mixture that has been allowed to undergo hydration reactions and has been given time to cure. The lime-ash mixture in GLASH was neither given time to cure nor water to begin hydration reactions. This is important because it is believed that hydration reactions lead to an increased surface area of the ash due to the formation of zeolitic materials such as ettringite and other calcium silicate hydrate phases which have a larger surface area compared to fly ash spheres. Adding the waste material to this may yield completely different results from those found in this study. This is actually another area of research worth looking at.

There is an opportunity for improving the stabilisation of organic hydrocarbon sludges with fly ash by optimising the waste-binder mixing ratio. The pH can be used as an indicator in which a highly alkaline pH signifies an excess of the binder. This follows the idea that while using ash to treat the waste with respect to flammability and volatility and mobility of organic contaminants, the hydrophobic nature of the waste can be used to lower the leachability of inorganic constituents. A proper balance of these two synergistic processes could lead to a much improved stabilised product.

Time and effort could be saved by basing the choice of a binder system on the primary or dominant stabilisation process. For instance, addition of lime would be beneficial if solidification or physical entrapment is a dominant stabilisation process. If adsorption is dominant, such as believed to be in the current study, then lime addition would be beneficial only if the lime has superior binding capabilities compared to ash, or if it has preferential affinity for specific constituents which fly ash fails to stabilise. Otherwise there is no evidence that lime directly affects the binding capabilities of ash. It merely acts as a binder within a binder while other additives, such as surfactants, are believed to directly affect the adsorption qualities of a binder, hence improving its effectiveness.

CHAPTER FOUR

4. MOBILITY OF CONTAMINANTS FROM THE STABILISED PRODUCT

4.1 Introduction

One of the major problems facing disposal of treated hazardous waste by landfill is the possibility of groundwater contamination by toxic constituents that may leach out of the dump site. Highly mobile species have a better chance of reaching groundwater, resulting in contamination. This is one of the areas that stabilisation/solidification (S/S) is trying to address, in order to minimise the mobility of undesirable constituents within a hazardous waste.

The mode in which "immobilisation" is achieved is described in section 2. The term immobilisation may be misleading in a sense that, in cement and pozzolanic systems, true immobilisation is not generally achieved in practice; reduced mobility is what is normally achieved instead.

In the S/S of inorganic waste, solidification and stabilisation can be effected at the same time using normal reagents such as lime and Class F or Class C fly ash. However, as has been described in section 3, the stabilisation of organic oily sludges containing hydrocarbons can hardly be based on solidification. It is better to aim at a form of stabilisation in which adsorption plays a major role. Ironically, while oily waste would generally not contain inorganic elements, at least to appreciable levels, it is the inorganic elements that eventually become a concern when organic waste is stabilised using cement-based S/S systems.

In this chapter this reality is explored and attempts are made to understand the mechanics involved. The mobility of organic constituents was not given much attention due to analytical costs involved in organic analysis as well as the scope and timeframe of this work. An attempt was made to identify elements of concern through the calculation of their estimated environmental concentration (EEC) and comparing this to the acceptable risk level (ARL) in each case based on the Minimum Requirements. A short discussion was presented on the potential impact of the S/S treated waste in the event of it being disposed of by landfill as well as

the relevance of legal requirements in the evaluation of the success of S/S as described by the Minimum Requirements document (Department of Water Affairs and Forestry, 1998).

4.2 Analytical methods

4.2.1 Saturated paste extracts

4.2.1.1 Ash

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (352.55g) was mixed with distilled water (162 ml) to achieve a saturated paste. The paste was left overnight to allow the pore water to approach near-equilibrium concentrations. The paste was filtered under suction to acquire the extract, which was subsequently filtered through a 0.45µm filter to exclude most of the suspended matter. The pH and electrical conductivity of the extract were measured and the samples were diluted to an electrical conductivity of below 100 µS/cm and analysed for major cations and anions by IC and trace elements by ICP-MS.

4.2.1.2 LASH

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (225g) was mixed with slaked lime (25g) and distilled water (116 ml) to achieve a saturated paste. The paste was left overnight to allow the pore water to approach near-equilibrium concentrations. The paste was treated as described above (4.2.1.1).

4.2.1.3 GASH

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (257g) was mixed synthol gunk (52g) and distilled water (85 ml) to achieve a saturated paste. The paste was left overnight to allow the pore water to approach near-equilibrium concentrations. The paste was treated as described in section 4.2.1.1.

4.2.1.4 GLASH

A sample of ash was air dried for a day and sieved through a 2 mm sieve. The sieved ash (231.3g) was mixed synthol gunk (52g), slaked lime (25.7g) and distilled water (100 ml) to achieve a saturated paste. The paste was left overnight to allow the pore water to approach near-equilibrium concentrations. The paste was treated as described in section 4.2.1.1.

4.2.2 leaching of the less than 2 mm fraction

A standard DIN 418 water leaching test and a standard TCLP acid leaching test were used to leach samples of LASH, GASH and GLASH. The DIN 418 standard test uses distilled water and a fraction of the solid sample sieved through a 2 mm sieve. The TCLP test uses a solvent prepared by diluting 5.7 ml of glacial acetic acid to a litre with deionised water to achieve a pH of 2.85. The normal TCLP test is carried out on material sieved through a 9 mm sieve, but in this case a 2 mm sieve was used for easy comparison with the DIN 418 leach test. This is, incidentally, a more conservative approach. All waste formulations were tested as follows:

A solid sample of the waste (1.5g) was mixed with the leaching solution (30 ml) in a 50 ml centrifuge tube. The resulting suspension was stoppered with a stopper which was covered with parafilm and shaken on a reciprocal shaker for 24 hours. The suspension was then filtered through a 0.45μm filter and analysed for chemical constituents and trace elements.

4.2.3 Leaching of pellets

Pellets of LASH, GASH and GLASH, prepared as described in section 3, were leached with distilled water and the TCLP solution. Each pellet (approximately 10g) was fixed in a 500 ml plastic container using a fast acting adhesive. After the pellets were secured, they were equilibrated with 200 ml of the leaching solution for 24 hours at a slow shaker speed to avoid displacement of pellets from their fixed positions. The solution was filtered through a 0.45μm filter and analysed for chemical constituents and trace elements.

4.2.4 Micro-structural analysis of pellets

After leaching of the pellets was complete, they were dried at ambient temperature and each pellet was broken into 4 pieces of which one piece was used for SEM-EDS analysis. Pellets

were placed under high vacuum overnight to remove water residues. They were then mounted, three at a time, on metal slides and coated with amorphous carbon to produce sample conductance. SEM images were collected using the LEICA StereoScan 440 SEM-EDS system at 15kV with a beam current of 111pA and a take-off angle of 35 degrees. EDS spectra were recorded for selected crystal structures. A reference analysis was also performed on samples that were not exposed to leaching solutions.

4.3 Results and Discussion

4.3.1 Saturated paste extracts

A chemical analysis of the aqueous extracts obtained from the saturated pastes of Ash, LASH, GASH and GLASH is given in Table 4-1.

Table 4-1: Chemical analysis of the saturated paste extracts of Ash, LASH, GASH and GLASH. The major ions were identified by IC.

Analysis (mg/l)	*Ash*	*LASH*	*GASH*	*GLASH*
pH	12.83	12.85	12.55	12.86
EC(mS/cm)	18.3	18.2	12.1	17.2
SAR	16.4	18.9	34.1	11.9
DOC	136	102	682	388
Li	10.0	11.0	9.0	6.0
Na	1678	1723	1877	1412
K	378	496	409	325
Mg	30	7.0	7.0	20
Ca	536	437	156	729
F	43.2	25.9	21.8	36.3
Cl	536	428	631	469
NO_2	BDL	BDL	BDL	BDL
Br	BDL	BDL	BDL	BDL
NO_3	102	102	BDL	104
PO_4	27.1	BDL	BDL	BDL
SO_4	232	167	587	202

BDL below detection limit

The data suggest that the pore solution of the stabilised products (GASH and GLASH) is highly alkaline. This alkalinity is due to the excess of the binder and is observed across the various treatments with pH values ranging between 12.55 and 12.86. These high pH values would maintain a net negative charge on DOC. This charge will have to be balanced by cations in the system. It is because of this reason that the organic waste is expected to have an effect on cationic components of the binder. Table 4-2 suggests that this is actually happening when one considers the highly elevated Al and Si levels in GASH and GLASH. If these high Al levels were due to the amphoteric nature of Al, then all the extracts would be expected to show elevated Al concentrations since they are all highly alkaline. But this is not the case: the Al (as well as Si) show significant leachability in the treatment containing synthol gunk.

Table 4-2: A quantitative ICP-MS trace element analysis of the saturated paste extracts of Ash, LASH, GASH and GLASH.

Analysis (mg/l)	*Ash*	*LASH*	*GASH*	*GLASH*	*% error*
Al	2.49	1.47	20.45	16.90	0.38
Si	14.80	8.65	18.50	18.19	
Cr	BDL	BDL	0.28	BDL	15.0
Mn	0.04	0.02	0.05	0.17	6.17
Fe	2.31	BDL	BDL	1.61	16.3
Ni	0.19	0.08	0.74	0.16	5.47
Cu	0.37	BDL	0.38	0.28	2.46
Zn	0.43	0.20	0.83	0.06	-11.5
Br	3.38	2.42	4.53	2.68	
Se	0.37	0.24	0.28	0.10	-1.09
Rb	1.16	1.01	0.64	0.75	1.00
Sr	39.30	48.70	5.44	52.50	5.80
Mo	0.41	0.17	1.21	0.22	5.03
Cd	0.04	BDL	0.03	BDL	5.22
Ba	3.90	5.32	BDL	4.50	6.08
Pb	0.44	0.35	1.87	BDL	6.78

BDL below detection limit

The presence of lime ($Ca(OH)_2$) in the stabilised product (GLASH) appears to improve the stabilisation of DOC from a leachability of 681.5 mg/l in GASH to 388 mg/l in GLASH. The mechanism leading to this reduction in DOC is not properly understood. This reduction, however, suggests that functional groups that are preferentially precipitated or flocculated by lime are part of the DOC from the GASH extract. The DOC (388 mg/l) still in solution in the

extract from GLASH may possibly to be composed of stable metal complexes (especially Al complexes) and organic material that cannot be precipitated by lime.

The argument of DOC being precipitated by lime may provide an explanation for both the low calcium leachability in GASH as well as the low DOC in LASH (101.5 mg/l) compared to that in Ash (135.5 mg/l). The high sulfate content in GASH leachate (586.8 mg/l) may be indirectly due to the removal of Ca from solution by organic matter. Hence sulfate cannot be precipitated as gypsum and remains in solution.

The electrical conductivity of GASH (12060 μS/cm) is the lowest of all the extracts, which does not seem to reflect the elemental composition of GASH relative to the other extracts as determined by IC and ICP-MS. A possible reason for this low EC in GASH is its high DOC. The DOC is believed to be composed of a variety of negatively charged organic compounds which may possess a variety of functional groups and may assume various sizes. This often results in bulky complexes, especially with trivalent cations, which are poor electrolytes due to their sluggish migration within the solution. These complexes may even be neutral but still remain in solution, in which case they would not take part in electron transport, instead they crowd the conducting solution and hinder the migration of potential electron carriers. This would lead to EC suppression in GASH being more significant than in the other treatments. Furthermore, the dominance of sulfate in GASH may result in increased solubility of the $CaSO_4^0$ ion pair. This will result in a lower EC for a given ionic strength.

The concentrations of Ca, Al, Si and SO_4 in the LASH extract are all relatively low (Ca is quite low considering the fact that it was manually added in LASH but it still remains lower than in Ash). These are, coincidentally, all components of ettringite, which was not detected by XRD possibly because the ash used was not Ca-enriched (Fey *et al*, 1999). Nevertheless, the decrease in the concentration of these four ions in the presence of lime suggest a formation of some form of a pozzolanic by-product which removes these components from solution . The presence of synthol gunk appears to inhibit this process, resulting in increased calcium leachability in GLASH. This should be expected if Al and Si, which are necessary for the formation of insoluble CSH (calcium silicate hydrate) phases, are locked into stable complexes by DOC and are therefore unavailable for pozzolanic reactions.

Indications of binder excess in this study are the highly alkaline pH and the high calcium in the extract from GLASH.

The potential implications of complex formation between Al, Si and DOC are increased leachability of Si and Al from the stabilised product. Many organic complexes, especially chelates, are particularly stable in natural environments. Their breakdown would be induced by either very strongly oxidising conditions, which are not common in natural systems, or anaerobic processes which will facilitate the breakdown of the organic ligand.

The complexed trace element would, as a result, travel longer distances than it would under normal circumstances. This increases the chances of the complexed trace elements reaching groundwater and migrating long distances underground in a relatively inert form. While this can result in dilution, the possibility exists of a localised precipitation of the trace elements when complexes reach a zone with conditions favouring complex breakdown, resulting in a zone rich in, for instance, Al. If the organic complexes exhibit toxicity characteristics, problems within aqueous ecosystems may be experienced and the mobility of the complexes would ensure that a larger area is affected.

Strontium shows a clear trend of decreased solubility in GASH relative to all the other treatments. This behaviour is consistent for all leaching tests performed (saturated extracts, < 2mm fraction, and pellets) and may be due to precipitation of Sr in the form of a sulfate salt.

4.3.2 Distilled water leach test

According to the chemical analysis of the distilled water leachate given in Table 4-3, GASH has the best leachate quality compared to that of the other waste materials. Most of the arguments already given to describe the leaching behaviour of contaminants from the saturated paste extracts appear to be still relevant in this 1 : 20 water leaching test.

The lower pH in GASH is an indication of a lower degree of binder saturation, while GLASH has a higher pH which can be attributed to the addition of slaked lime. The slaked lime was laboratory grade and much more finely divided than fly ash probably due to it being pulverised before being sold. This increases its binding surface area, which explains the more alkaline pH in GLASH.

Table 4-3: Chemical analysis of water extracts from the sieved samples (less than 2mm) of Ash, LASH, GASH and GLASH. The major ions were identified by IC.

Analysis (mg/l)	*LASH*	*GASH*	*GLASH*	*Gunk*
pH	12.38	11.08	12.33	7.41
EC(μS/cm)	6145	587	6340	609
Total Alkalinity	1835	173	1904	86
DOC	7.4	19.6	19.5	–
Li	0.6	0.1	0.3	BDL
Na	44	29	53	24
NH_4	1.7	0.3	1.5	6.9
K	30	10	15	22
Mg	7.0	1.0	5.6	2.0
Ca	935	87	824	114
F	BDL	0.4	0.5	2.9
Cl	33	16	29	4.3
NO_2	BDL	BDL	BDL	0.4
Br	BDL	BDL	BDL	BDL
NO_3	BDL	BDL	BDL	0.4
PO_4	BDL	BDL	BDL	BDL
SO_4	BDL	41	17.2	171

BDL = below detection limit

Variations in electrical conductivity appear to be consistent with variations in the Ca^{2+} concentration. The hydroxyl anion is believed to be the dominant counter ion for Ca since the interaction of the system with atmospheric CO_2 is assumed to be minimal because the samples were stoppered. The OH^- ion is therefore contributing largely to the electrical conductivity due to its large specific conductance. The EC drops sharply when Ca^{2+} is removed from solution as seen in the leachate from GASH.

The mobility of Ca, and to a lesser extent Mg, in GASH appear to be decreased probably due to the presence of gunk as was observed in the saturated extracts. The data suggests that there is no benefit in adding lime to the stabilised material with respect to immobilisation of organics since the amounts of DOC in GASH (19.6 mg/l) and in GLASH (19.5mg/l) are practically similar. This is contrary to the observations in the saturated paste extracts. The likely reason is that the saturated paste extract is concentrated, and hence differences in contaminant mobility within a sample may be exaggerated.

The most effective use of lime would be achieved if lime can stabilise organic compounds that cannot be stabilised by ash alone. It may be worthwhile to identify organic components that leach out of the stabilised material in the presence of lime as well as its absence. The DOC that leaches out of GASH and GLASH is approximately 2.5 times higher than in LASH, which is better than observed in the saturated paste extracts.

A significant difference between the saturated paste and the standard leaching tests performed here is that the saturated pastes were open to the atmosphere, while the standard leaching tests were performed in stoppered containers with the headspace less than a third of the total volume of the container. Carbonate precipitation in the saturated paste may be responsible for the much lower Ca content in the saturated paste extracts. Because the sample in the DIN 418 leaching test is stoppered, the interaction with the atmosphere is limited and could be attributed to the high Ca content in the leachate due to lack of carbonate anions which would precipitate Ca as calcite.

Leachate from GASH still shows a high sulfate content when compared to the others. A comparison between Gunk and the other three leachates (LASH, GASH and GLASH) should be done with caution because for Gunk, a 10 parts water to 1 part solid extraction was performed. This was done specifically to get an extract concentrated enough for the trace elements to be detectable. The SO_4 and Ca in Gunk are unexpectedly high, implying the presence of gypsum in Gunk. Previous work (Ginster *et al.*, 1999) does not show the same high sulfate content in Gunk, hence this is thought to be due to gypsum contamination and the source is unknown. Sulfates in LASH were below the detection limit of the IC due to the high dilution required to adjust the Cl concentration to within the IC detection range.

The inclusion of gunk into Ash appears to decrease the solubility of Si (Table 4-4). This effect is not observed in the presence of lime (in GLASH). It is possible that Si is involved in stabilisation/solidification reactions involving synthol gunk. If in these reactions lime is the preferred binder, then it would be expected for Si to be more soluble in the presence of lime, since lime would be utilised instead and Si would behave in a similar manner as it does in the absence of Gunk.

Table 4-4: A quantitative ICP-MS trace element analysis of water extracts from the sieved samples (less than 2mm) of Ash, LASH, GASH and GLASH.

Analysis (ppm)	*LASH*	*GASH*	*GLASH*	*Gunk*
B	4.76	0.45	5.92	0.01
Al	6.83	5.46	6.96	0.05
Si	77.3	6.87	66.1	1.13
Cr	0.09	0.05	0.17	0.01
Mn	0.04	0.001	0.20	0.45
Fe	2.44	0.23	2.73	0.33
Ni	0.05	0.01	0.05	0.02
Cu	0.05	0.01	0.06	0.01
Zu	0.33	0.003	0.27	0.07
Br	2.83	0.55	1.29	0.14
Sc	0.01	0.01	0.01	0.001
Rb	0.11	0.01	0.02	0.004
Sr	17.9	2.74	4.93	1.05
Mo	0.13	0.03	0.04	0.05
Cd	0.002	BDL	0.002	BDL
Ba	8.14	0.14	1.63	0.03
Pb	0.04	0.002	0.02	0.01

Apart from SO_4^{2-} and F^-, all chemical constituents in the leachate from GASH are present in lesser quantities than in the leachate from LASH. This uniform behaviour of all chemical constituents, including trace elements, suggest the possibility of a physical process being responsible for the decrease in leachability. Since solidification (formation of a monolith) was not achieved, the physical process more likely to be responsible for the decrease in leachability is hydrophobicity. The hydrocarbon rich gunk can coat fly ash particles and clusters forming a hydrophobic layer which limits water access and hence the resulting low leachability. This can be formally referred to as the hydrophobic stabilisation of inorganic ions from the binder by the hydrocarbon material from the organic waste. If this argument is true, then the particle size of fly ash is of major importance in the treatment of oily hydrophobic waste. The problem with oily waste is that it does not dissolve fly ash grains and conglomerates when it comes into contact with them, it simply coats them. Hence, a smaller particle size would be more effective than a larger particle size.

The method used for the determination of particle size was performed in an aqueous medium . Thus, results from this method are more likely to indicate a particle size smaller than the

"active" particle size of the ash. The active particle size in this context can be defined as the particle size of fly ash particles before their partial dissolution in water. This definition is only applicable in this context where a hydrocarbon rich organic waste is stabilised using a pozzolan or cement system.

The poor quality of leachate from GLASH with regard to trace elements and major ions, except for SO_4^{2-}, when compared to the leachate from GASH suggests that, contrary to expectations, the addition of excess binder during stabilisation leads to a deterioration of leachate quality. There seems to be a need to balance the adsorption of organic components by the binder with the hydrophobic protection of inorganic contaminants from leaching by the organic waste. This can be done by adding just enough binder in the system with pH and EC values being used as crude indicators of binder excess.

Apart from DOC, SO_4^{2-} and F^-, the water leach data (Table 4-3) suggest that GASH will have a less severe effect on the environment compared to limed ash. This is important because the bulk of inorganic ions originates from ash, and not from synthol gunk. By implication, a synergistic relationship between fly ash and synthol gunk exist in which the ash stabilises the gunk by improving its ease of handling and its flammability, while the synthol gunk lowers the leachability of inorganic ions from ash by forming a hydrophobic layer around ash particles and hence limiting access of water.

4.3.3 TCLP leach test

The TCLP was developed to assess the effects of co-disposing hazardous waste with general waste. The decomposition of organic waste has the potential to produce organic acids, which will affect the mobility of inorganic elements. In this study the hazardous waste is synthol gunk and the general waste is fly ash.

The acidity of the TCLP extraction solution lowers the alkalinity of the waste formulations. This is suggested by the lower pH values of the TCLP extracts (Table 4-5) when compared to those found from the DIN 418 standard leach test. GASH has the lowest acid neutralising capacity as shown by the low pH of the extract (6.64). This low pH in GASH has a potential to affect the mobility of other ions, as will be seen with Al.

Table 4-5: Chemical analysis of TCLP extracts from the sieved samples (less than 2mm) of Ash, LASH, GASH and GLASH. The major ions were identified by IC.

Analysis (mg/l)	*LASH*	*GASH*	*GLASH*
pH	11.47	6.64	10.77
EC(μS/cm)	5565	4755	5050
Total Alkalinity	3058	2860	2917
Li	0.7	0.7	0.3
Na	38	45	39
NH_4	1.4	2.7	2.0
K	18	19	15
Mg	16.2	211	12.2
Ca	2186	2024	2448
F	311	324	318
Cl	34	47	47
SO_4	6.0	296	142

The high alkalinity and EC can be largely attributed to the acetate anion. It was observed during alkalinity titrations that TCLP samples had a pH buffer zone between pH 6 and pH 5, which is approximates the pKa region of acetic acid. This explains why the alkalinity of GASH is comparable to that of GLASH despite their significant differences in pH. The major contributor to the high EC is expected to be Ca. It is believed that calcium is retained in solution as $Ca(CH_3COO)_2$, hence the elevated concentrations in the TCLP extracts.

The high solubility of F^- on all TCLP extracts was unexpected, it is possible that the IC instrument misinterpreted the F^- peak for the acetate peak since the two peaks occur quite close to one another. The F^- concentrations are, therefore, expected to have a highly positive systematic error.

The TCLP extraction appears to affect more strongly divalent cations (Mg and Ca) with the net result of making them more mobile. The mobility of sulfate is also largely affected by acidic conditions, probably from the dissolution of gypsum, which may lead to more Ca into solution.

Because of the strong complexing capabilities of Al, it would be expected that a TCLP leach should release more Al into solution. However, due to the low pH of the TCLP leachate from GASH, the solubility of Al appears to be much reduced (0.4 ppm) as shown Table 4-6

compared to its solubility in distilled water (5.46 ppm). This means that by carefully controlling the amount of binder, the alkalinity of the stabilised waste formulation can be controlled and this will have implications on solubility of Al depending on the final pH of the leachate. Other elements that appear to follow a similar trend of reduced solubility upon TCLP extraction include B, Si and Br in LASH; B and Si in GLASH. This trend is shown by Al in all extracts.

Table 4-6: A quantitative ICP-MS trace element analysis of TCLP extracts from the sieved samples (less than 2mm) of LASH, GASH and GLASH.

Analysis (ppm)	*LASH*	*GASH*	*GLASH*
B	0.51	5.23	2.20
Al	0.61	0.40	0.41
Si	13.9	45.6	7.88
Cr	0.21	0.17	0.19
Mn	0.08	4.91	0.07
Fe	6.72	5.10	7.30
Ni	0.14	0.21	0.17
Cu	0.14	0.05	0.29
Zn	1.25	0.88	1.00
Br	0.87	5.49	2.72
Se	0.04	0.03	0.04
Rb	0.09	0.02	0.02
Sr	24.6	39.0	20.6
Mo	0.16	0.10	0.08
Cd	0.003	0.004	0.004
Ba	7.38	0.85	1.89
Pb	0.03	0.02	0.05

Strontium and Fe on the other hand appear to have increased solubility when exposed to TCLP extraction conditions. Strontium was observed to be stabilised by the GASH in the distilled water extracts. The TCLP extract information suggests that Sr may be released if GASH is exposed to acidic media. Even if the alkalinity is high enough not to be effectively neutralised as seen in LASH and GASH which are still highly alkaline at pH 11.47 and 10.77, respectively.

4.3.4 Expected environmental concentration (EEC)

The calculation of the EEC was performed in an attempt to identify those constituents that pose a risk to the environment. It was calculated according to the definition given by the Minimum

Requirements (Department of Water Affairs and Forestry, 1998) and was compared to the acceptable risk defined as 10% of the LC_{50} of the waste constituent.

The EEC values given in Table 4-7 were calculated on the assumption that 245000 tons of synthol gunk requires treatment and the disposal of the treated material will take place over a period of 100 months on an area of 40 Ha.

The EEC calculations for LASH and Gunk were based on a total quantity of 245000 tons which requires disposal. For GASH and GLASH the mixing ratio of 1 gunk to 6.67 stabilised product was taken into account and the final quantity of waste requiring disposal was thus calculated to be about 16 million tons.

Manganese appears to be the only element of major concern in synthol gunk. Strontium, however, does approach the AR (acceptable risk) value and may be referred to as the element of second-most concern. GASH and GLASH show unacceptable leachability of Al and Sr. However LASH, which can arguably be referred to as a general waste, also shows excessive leaching of the same elements. Ash is believed to be the major source of these two elements. The EEC of Al in GASH and in GLASH is much higher than in LASH due to the increased total load when the two waste materials have been combined. The inclusion of lime in the stabilised product (GLASH) appears to have negative effects with regard to mobility of trace elements such as Mn, Fe, Cu, Zn, Ba and Pb. Ba, while not exceeding the AR in LASH, is also a concern at 6581 ppb, which suggests that lime has an effect of enhancing the leachability of Ba. The increased mobility of the other elements seem to be related to the presence of both lime and synthol gunk. According to Table 4-7, LASH, GASH and Gunk are all HR2 (hazard rating 2) while GLASH is HR1. Elements that determine the hazard rating and hence the type of landfill necessary for the safe disposal of the waste are enclosed in brackets. Cd in GLASH does not delist because for an HR1 waste to delist, the EEC must be a hundredth of the LC_{50}.

Table 4-7: Comparison of the acceptable risk with the estimated environmental concentration (EEC) of LASH, GASH, GLASH and Gunk for the distilled water extraction.

Analysis	*ARL (ppb)*	*LASH (mg/l)*	*EEC (ppb)*	*GASH (mg/l)*	*EEC (ppb)*	*GLASH (mg/l)*	*EEC (ppb)*	*Gunk (mg/l)*	*EEC (ppb)*
Al	390 (2)	6.832	276.15	5.457	220.6	6.959	281.3	0.045	1.8
Cr	4700 (3)	0.085	3.45	0.0495	13.35	0.1715	46.15	0.0115	0.45
Mn	300 (2)	0.035	1.4	0.001	0.25	0.2015	54.3	0.4495	18.15
Fe	9000 (3)	2.436	98.5	0.226	60.9	2.7285	734.75	0.333	13.45
Ni	1140 (2)	0.0525	2.15	0.0105	2.9	0.0465	12.5	0.019	0.75
Cu	100 (2)	0.0525	2.1	0.0145	3.9	0.055	14.75	0.0045	0.2
Zn	700 (2)	0.333	13.45	0.003	0.85	0.2655	71.5	0.073	2.95
Se	260 (2)	0.0095	0.4	0.009	2.4	0.0115	3.15	0.0005	0.05
Sr	1000 (3)	17.879	722.75	2.736	736.75	4.9345	1328.7	1.05	42.45
Cd	31 (1)	0.0015	0.05	0	0.05	0.002	0.5	0.0005	0
Ba	7800 (3)	8.14	329.05	0.139	37.5	1.6295	438.8	0.034	1.4
Pb	100 (2)	0.035	1.4	0.002	0.5	0.0205	5.55	0.007	0.25

Values in brackets denote the hazard rating of the corresponding element.

Elements of concern in GASH are the same for the TCLP and the DIN418 leach tests. Only the EEC values differ, with the TCLP leaching less Al and much more Cu, Zn, Fe and Sr among others as shown in Table 4-8. The TCLP extract of LASH shows Cu and Zn as new elements that were previously not leached by the distilled water leach test. More new elements that are mobile in acid conditions are observed in GASH. These include Mn, Fe, Ni, Cu and Zn. Some of these elements may owe their enhanced mobility to the slightly acidic conditions of the GASH extract (pH 6.64) while others may be complexed by the acetate anion into solution. According to the data in Table 4-8, the classification of LASH remains HR2 but now with Zn as the most excessive element. GASH and GLASH are now HR1 because of Cd, which does not delist because its estimated environmental concentration is more than a hundredth of its LC_{50}.

Table 4-8: Comparison of the acceptable risk with the estimated environmental concentration (EEC) of LASH, GASH and GLASH for the TCLP extraction.

Analysis	*ARL (ppb)*	*LASH (mg/kg)*	*EEC (ppb)*	*GASH (mg/kg)*	*EEC (ppb)*	*GLASH (mg/kg)*	*EEC (ppb)*
Al	390 (2)	0.61	24.6	0.4	107.5	0.41	110.25
Cr	4700 (3)	0.21	8.5	0.17	45.2	0.195	52.2
Mn	300 (2)	0.085	3.4	4.905	**1321.05**	0.065	17.75
Fe	9000 (3)	6.715	271.5	5.095	1372.05	7.3	1966.1
Ni	1140 (2)	0.135	5.55	0.21	56.85	0.175	46.65
Cu	100 (2)	0.14	5.65	0.055	14.4	0.29	78.35
Zn	700 (2)	1.255	50.75	0.88	236.4	0.995	267.85
Se	260 (2)	0.035	1.4	0.025	7	0.04	11.1
Sr	1000 (3)	24.63	**995.7**	39.045	**10513.7**	20.605	**5548.4**
Cd	31 (1)	0.005	0.15	0.005	1.1	0.005	1
Ba	7800 (3)	7.375	298.15	0.85	228.7	1.89	508.35
Pb	100 (2)	0.03	1.15	0.02	4.9	0.045	12.75

Values in brackets denote the hazard rating of the element.

4.3.5 Role of pozzolanicity of ash on solidification / stabilisation of organic waste

The criteria of choosing the binder for S/S related treatment procedure has been very much based on pozzolanic and cementitious abilities of the binder. This can be attributed to the fact that this technology was developed for the stabilisation/solidification of inorganic waste. It appears that this criterion of choosing the binder is not as applicable to organic waste as it is to inorganic waste.

One major problem is that true solidification can be hardly achieved when one uses a pozzolanic system to stabilise oily wastes. Hence the addition of solidifying agents would not be expected to improve the treatment process. Instead one may be faced with the reality of having to dump a much larger volume of waste (as seen with GASH and GLASH) where the volume itself has the effect of increasing the EEC of the elements and causing them to become an environmental concern. It appears that pozzolanicity does not play a major role in the treatment of organic waste, rather adsorption becomes a more important criterion to decide in the appropriate binder system.

The benefits of adding lime to ash in this study would be better evaluated against the effect it appears to have on the mobility of some of the trace elements. It is my opinion that a strong adsorbent of organic material would be better suited for the stabilisation of organic and oily sludges when added to ash.

4.3.6 Micro-structural analysis

Secondary electron images were taken at 300 X magnification to determine the general topography of the pellets. Results suggests that acid TCLP media are more aggressive towards LASH compared to distilled water as can be seen by the corroded TCLP leached pellet in Figure 4-1 C. The chemical analysis of the leachate given in Table 4-9 supports this observation and shows Ca to be leaching in larger quantities on leaching by the TCLP solution. Calcium is probably kept in solution as calcium acetate, the concentrations of the other anions are not enough to balance the positive charge due to Ca. Fluoride also appears to be leaching in large quantities, but as mentioned earlier, this could be due to the close proximity of the acetate and the fluoride peaks on the IC. The instrument is therefore mistaking the acetate anion peak (or part of it) to the fluoride peak. This is also suggested by the somewhat constant concentration of fluoride in all TCLP extracts, including those from the standard leach tests (< 2mm fraction).

Table 4-9: Chemical analysis of the DIN 418 and TCLP extracts obtained from the pellets of LASH, GASH and GLASH.

	Distilled water extracts			*TCLP extracts*		
Analysis (mg/l)	*LASH*	*GASH*	*GLASH*	*LASH*	*GASH*	*GLASH*
pH	11.92	10.08	11.66	4.87	4.11	4.77
EC(µS/cm)	1850	171	1220	3670	1810	3660
Li	0.2	BDL	BDL	0.5	0.4	0.5
Na	25.4	6.9	10.9	58.1	17.9	23.5
NH_4	0.6	0.1	0.4	1.5	0.8	1.5
K	12	4.3	5.5	32.6	30.9	4.1
Mg	0.8	0.6	2.3	32.7	61.3	112.7
Ca	55.7	21.6	211.3	**1446.4**	578.6	1416.8
F	1.3	BDL	0.5	312.2	238.7	272.8
Cl	10.5	7.1	7.2	22.9	18.7	34.0
NO_2	BDL	BDL	BDL	BDL	BDL	BDL
Br	BDL	BDL	BDL	BDL	BDL	BDL
NO_3	BDL	0.1	BDL	BDL	BDL	BDL
PO_4	BDL	BDL	BDL	BDL	BDL	BDL

SO_4	2.3	14.0	5.9	41.4	92.3	103.9

Figure 4-2 shows the same pellets studied in Figure 4-1 but at a higher magnification (10 000). Crystals shown in C were identified by EDS to be rich in Ca and O. These crystals were considered to be portlandite due to the lack of a prominent carbon peak in the EDS spectrum. Actually, the whole surface of distilled water leached LASH was covered in these crystals and this was thought to be due to re-crystallisation of portlandite through efflorescence once the pellet has been removed from distilled water. All other phases were therefore covered by crystals and could not be detected.

In contrast, TCLP-leached LASH shows exposed fly ash sphere and no evidence of portlandite re-crystallisation. The EDS spectrum shows Al, Si and O as dominant peaks, suggesting an alluminosilicate. The calcium is thought to be complexed by the acetate anion; hence the absence of portlandite crystals.

Secondary electron images (SE1) of dry pellets of GASH and GLASH shown in Figure 4-3 have a snowy appearance due to charging caused by non-conducting zones developed while bombarding the sample with electrons. These pellets were not exposed to any leaching environment, but they appear to have "weathering craters". Some of these "weathering craters" are an illusion due to charging of the sample. This emphasises the importance of comparing the leached samples with those that were not leached before making conclusions.

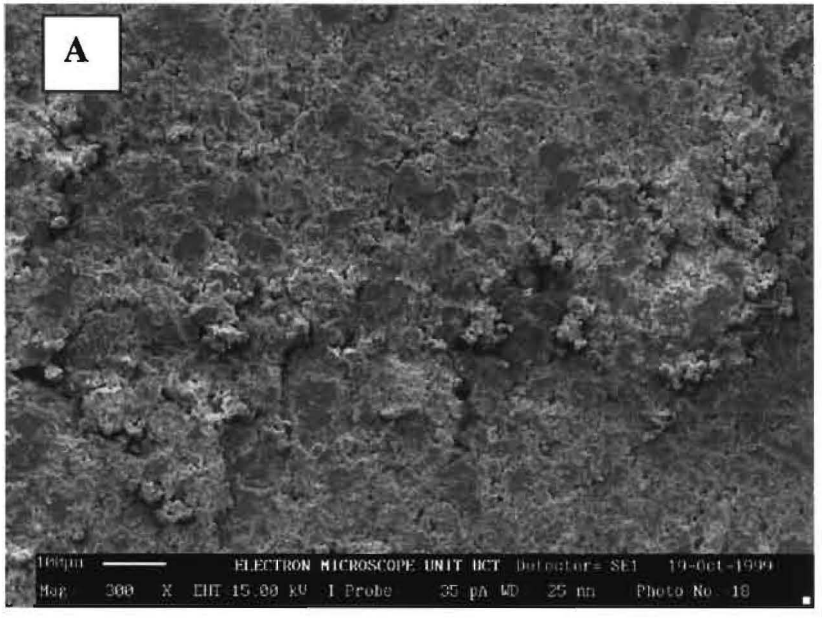
Secondary electron images shown in Figure 4-4 may be used to compare the leachability of LASH, GASH and GLASH pellets when placed in the TCLP solution 2. The LASH appears to be more aggressively leached than its gunk containing counterparts. It was therefore suggested that the gunk has a role of protecting ash against acid attack. The leach data (Table 4-9 and Table 4-10), however, do not support this suggestion. The suggested protection mechanism is hydrophobic micro-encapsulation of ash particles by synthol gunk. This could be observed at higher magnification (10 000X) as shown in Figure 4-5 together with an SE1 image of LASH, which lacks the gel-like gunk matrix observed in GASH and GLASH images. Photo C shows clean and exposed fly ash spheres on top of the gunk matrix suggesting that some acid attack has taken place. But, components of ash trapped within the gunk matrix were, most probably, left untouched by the acid. An EDS analysis of the matrix reveals that it is indeed a carbonaceous

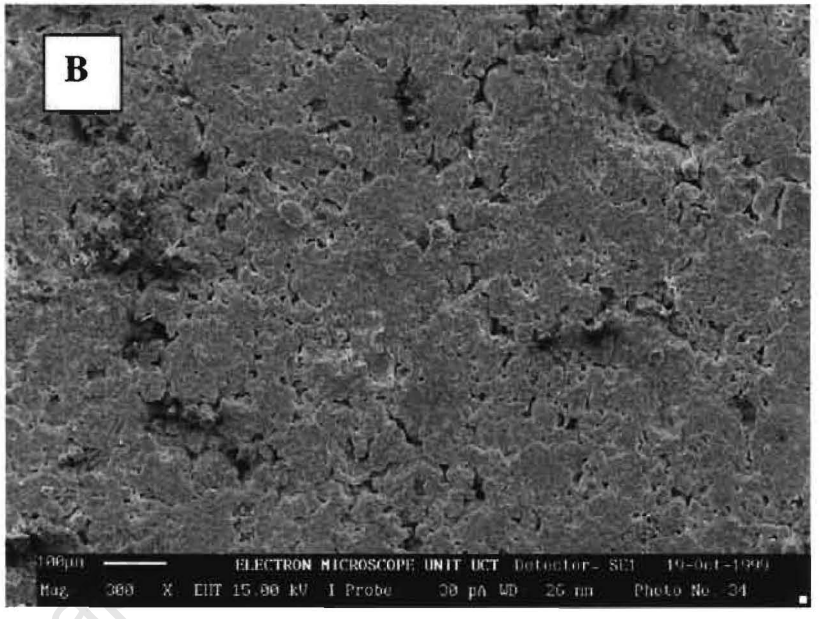
material impregnated by aluminous and siliceous material.

Table 4-10: Trace elements analysis of the DIN 418 and TCLP extracts obtained from the pellets of LASII, GASH and GLASII.

	Distilled water extracts			*TCLP extracts*		
Analysis (ppm)	*LASH*	*GASH*	*GLASH*	*LASH*	*GASH*	*GLASH*
B	0.22	0.02	1.64	0.84	1.67	0.88
Al	2.23	0.11	7.62	6.22	10.5	3.94
Si	8.97	1.19	23.8	29.3	23.1	23.4
Cr	0.05	0.002	0.18	0.15	0.13	0.06
Mn	0.02	BDL	0.01	1.68	1.43	1.63
Fe	0.57	0.02	0.83	3.47	2.23	2.54
Ni	0.01	0.001	0.01	0.07	0.06	0.26
Cu	0.02	0.001	0.02	0.07	0.06	0.12
Zn	0.07	0.01	0.05	0.86	0.36	0.69
Br	1.58	0.09	1.78	3.69	1.03	4.10
Se	0.01	BDL	0.03	0.02	0.01	0.01
Rb	0.15	0.001	0.03	0.17	0.01	0.01
Sr	7.18	0.08	6.76	21.2	10.9	12.4
Mo	0.02	0.002	0.06	0.01	0.02	0.10
Cd	0.001	BDL	0.001	0.01	0.002	0.004
Ba	1.41	0.01	0.46	5.00	0.76	1.47
Pb	0.01	0.001	0.01	0.02	0.03	0.08

BDL = below detection limit





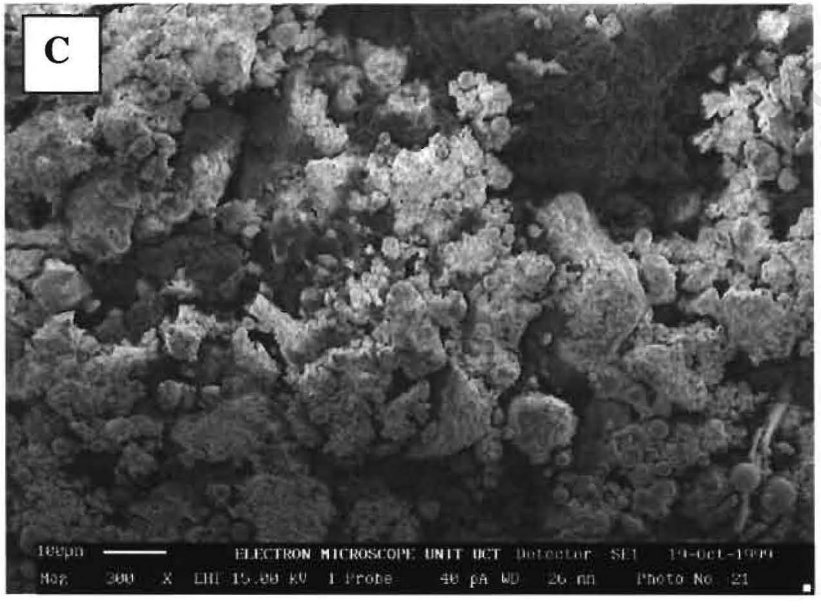
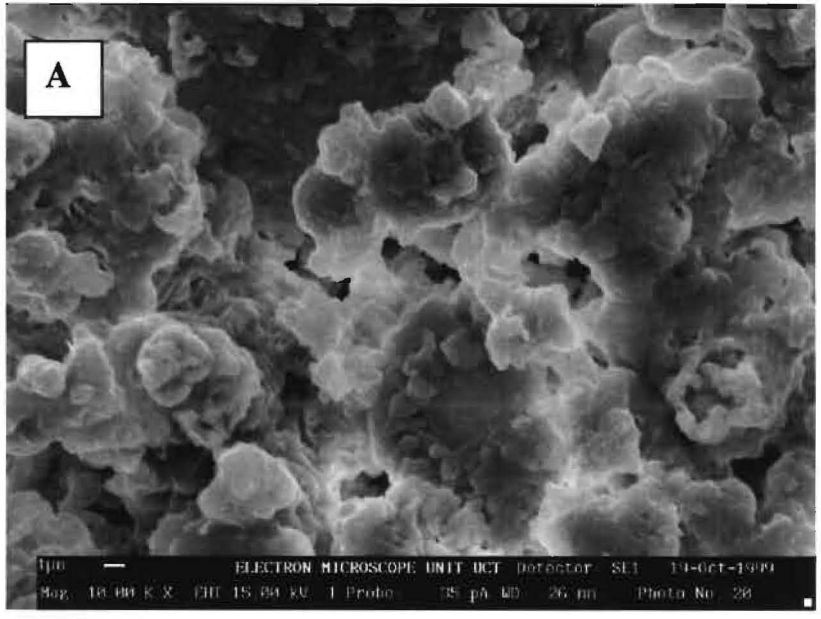
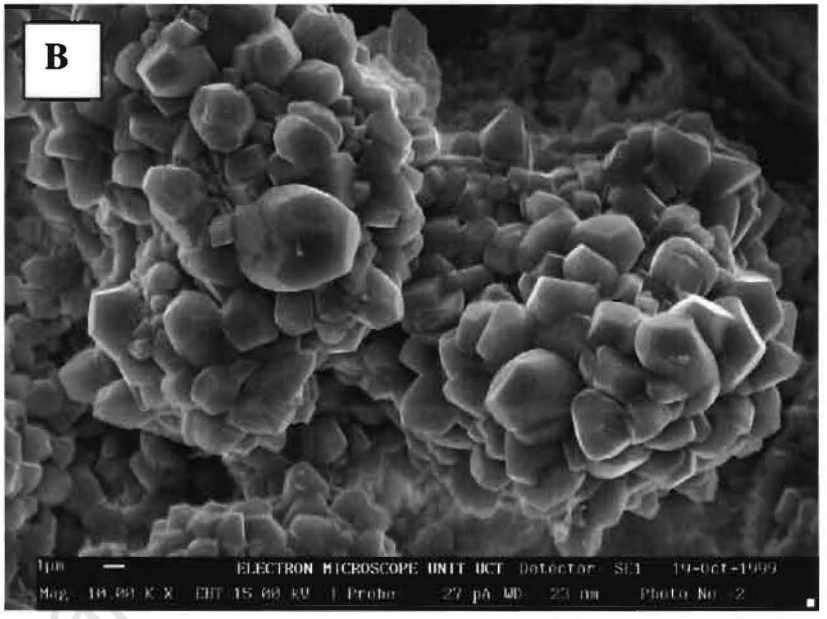


Figure 4-1: Secondary electron images of (A) dry LASH pellet that was not exposed to any leaching solvent, (B) LASH pellet that was leached in distilled water and (C) LASH pellet that was leached in the TCLP solution 2. All images are at 300 X magnification





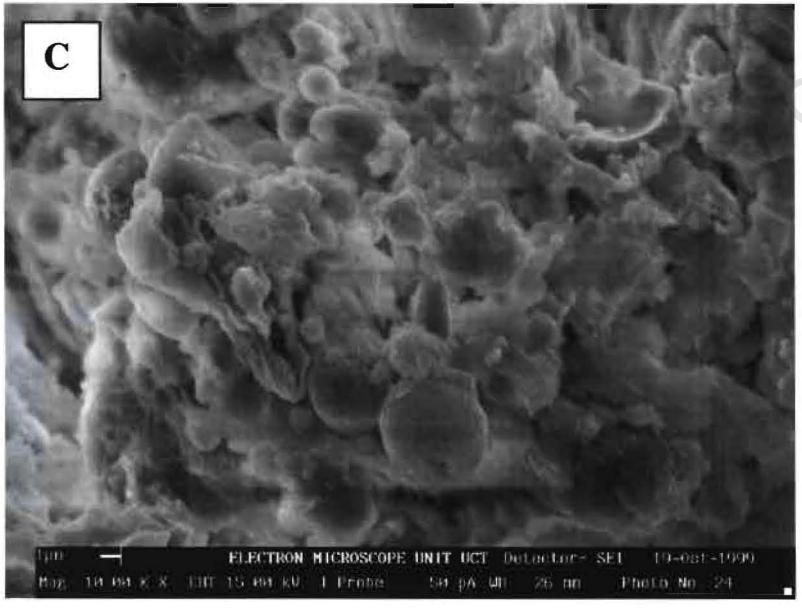


Figure 4-2: Secondary electron images of (A) dry LASH pellet that was not exposed to any leaching solvent, (B) LASH pellet that was leached in distilled water and (C) LASH pellet that was leached in the TCLP solution 2. All images are at 10 000 X magnification

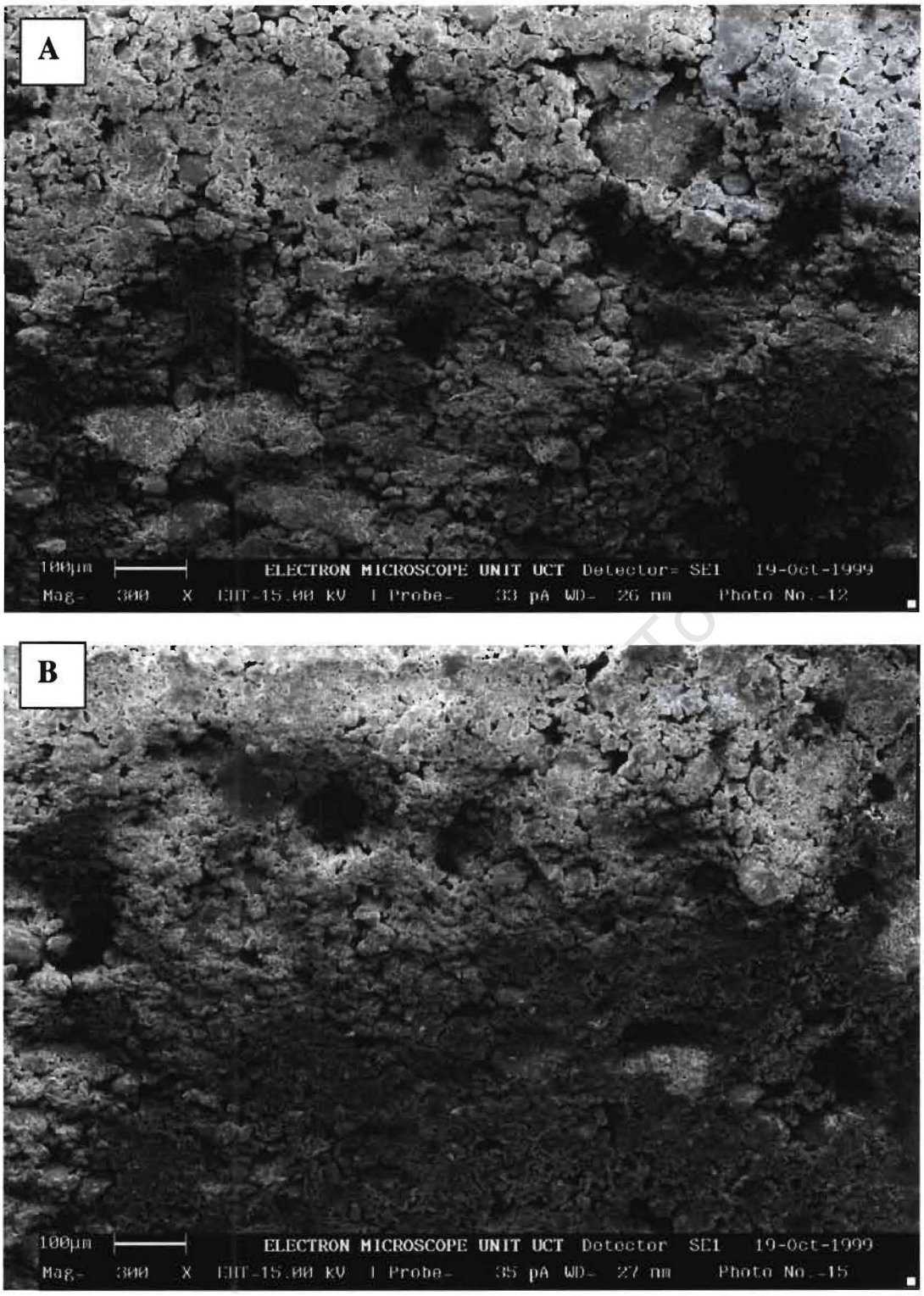


Figure 4-3: Secondary electron images of (A) dry GASH and (B) dry GLASH at 300X magnification showing "weathering craters" which are not due to leaching.

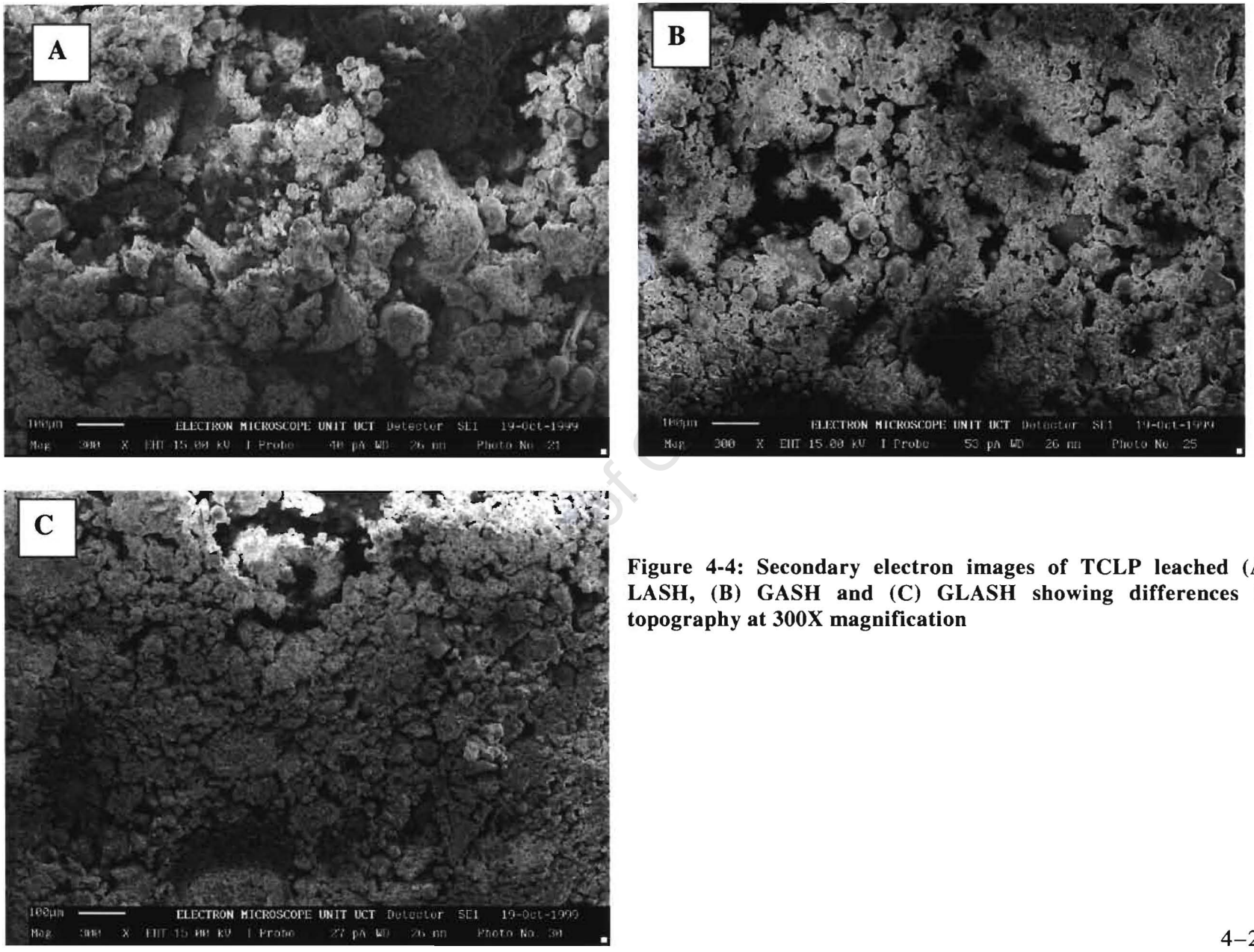
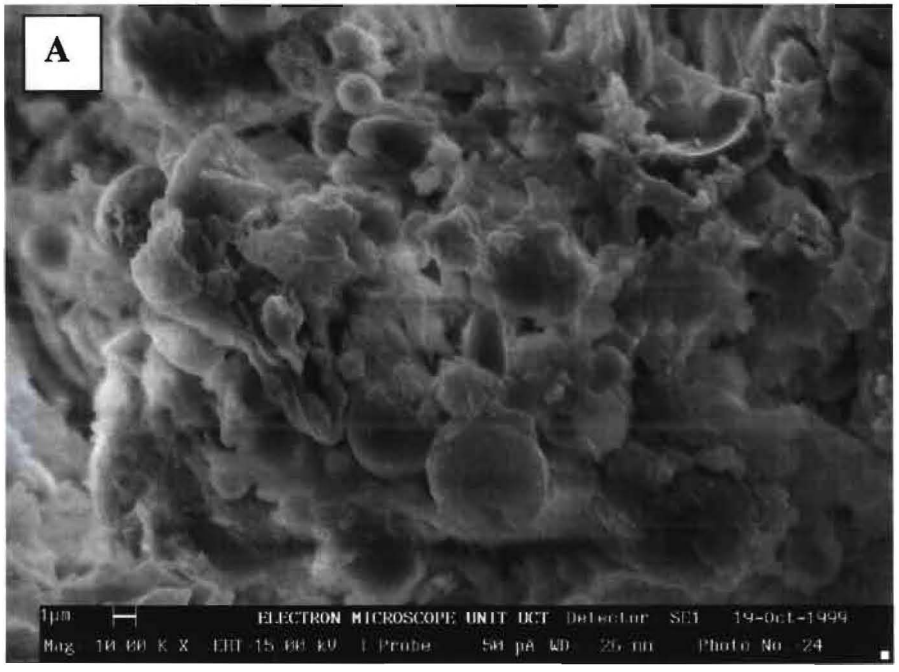


Figure 4-4: Secondary electron images of TCLP leached (A) LASH, (B) GASH and (C) GLASH showing differences in topography at 300X magnification



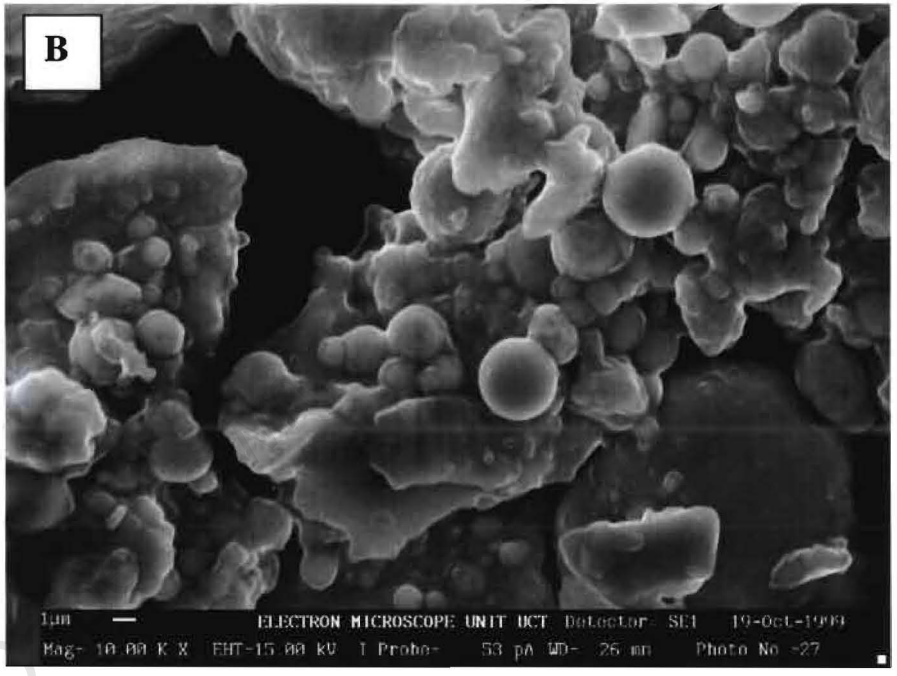


Figure 4-5: Secondary electron images of TCLP leached (A) LASH, (B) GASH and (C) GLASH showing the interaction of gunk with ash particles in the stabilised material. An image of LASH (A) is included for comparison.

4.3.7 Long-term stability of solidified/stabilised organic waste

Main concerns that may pose a threat to the long term stability of stabilised/solidified organic waste include volatilisation of the organic constituents. This can be facilitated by hot weather conditions. It is not understood whether this process will weaken or strengthen the stability of the stabilised waste. But it is more likely to take place and it is anticipated to have an effect on the stabilised product.

If the stabilised product is covered by some other material (such as coarse ash) to minimise aeolian distribution, the pressure of the overlying material on the stabilised product has the potential to squeeze out the oil from the product. This was observed when preparing pellets, and those pellets had an excess of binder but the oil was still squeezed out by applying pressure. An optimised stabilised product is expected to have less binder and should therefore be more sensitive to pressures.

Acid conditions, such as acid rain, can have an effect on the stabilised product as shown by the TCLP extraction. Manganese, Fe, Sr and Zn are among some of the trace elements that would be of concern under acid rain conditions (Table 4-8). The TCLP used here, however, assumes that acidity is produced by decomposition of organic matter to form organic acids rather than from carbonic acid from acid rain. Synthol gunk has not been reported to be digestible by micro-organisms to any appreciable extent. Perhaps this was due to the fact that it is generally not preferable to mix organic waste with inorganic waste and this is how synthol gunk has been kept, away from contamination by inorganic waste. For micro-organisms to grow, they need both organic and inorganic material, which will be the case in the stabilised product. This means that some biological activity may be expected within the stabilised product and it may lead to acid production.

4.3.8 Potential impact of land disposal of stabilised/solidified organic waste

The impact of the waste on land is a factor which depends largely on stability of the waste as well as environmental conditions associated with the disposal area. Potential elements of concern were identified in section 4.3.4 above. These are the elements that have a potential to contaminate ground water if the waste is landfilled. It appears that groundwater contamination is the primary impact that the stabilised/solidified waste can have on the environment.

During plant growth trials (discussed in the next Chapter) it was observed that cycles of wetness and dryness of the soil between watering lead to upward migration of salts by capillary action. These salts form a white layer, just like snow, of efflorescence on the soil surface. It is anticipated that this process may take place to a certain degree in the stabilised waste, unless good drainage is maintained, especially if clay barriers are considered for the disposal site.

4.3.9 Relevance of legal requirements on chemically stabilised / solidified waste materials

The waste classification system set out by the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste (Department of Water Affairs and Forestry, 1998) recognises the Toxicity Characteristic Leaching Procedure (TCLP) and acid rain test as appropriate leaching tests leading to the classification and possible delisting of hazardous waste.

These leaching tests are designed in an attempt to simulate worst case scenarios expected in field conditions, a conservative approach. While these tests, the TCLP in particular, are useful guidance tools in decision-making regarding the toxicity of waste material, the role which these tests play in waste classification, according to the Minimum Requirements document, requires that they are constantly reviewed and modified to accommodate advances in waste treatment technology as well as special cases.

The limitations of the TCLP in assessing the mobility of contaminants from S/S treated waste were pointed out by Poon and Lio (1997). Their concern was that cement-based S/S systems have a high acid neutralising capacity (ANC), which will eventually be exhausted when exposed to acidic conditions for a prolonged period. The TCLP does not take this into consideration since only one wash is performed regardless of the pH of the extract.

Data in Table 4-8 shows that according to the TCLP extraction, LASH, which is basically lime-doped fly ash, is actually a hazardous waste material. This immediately makes it difficult to justify results of a TCLP test on ash treated hazardous waste. According to this observation, the use of ash in the S/S technology in South Africa has a bleak future, unless modifications towards the application of the TCLP in cement and ash-based S/S procedures are conducted.

4.4 Conclusions

This chapter placed more emphasis on the mobility of trace elements from the stabilised product, with the prospect of groundwater contamination. It was observed that the synthol gunk has a tendency to make trace elements associated with the binder (ash or lime-ash mixture) more soluble, probably through complexation. A balance between the stabilisation of synthol gunk by ash and the hydrophobic protection of trace elements from ash by gunk from leach, even under acidic conditions, was thought to be a useful possibility in the optimisation of this S/S system.

According to the DIN 418, a distilled water leach test, the inclusion of slaked lime in the stabilised product results in Mn, Fe, Ni, Zn, Ba and Pb being leached to legally unacceptable levels. LASH appears as an H:H waste with hazard rating of 2 due to Al, this hazard rating remains the same when the TCLP is performed but is now due to Zn. It was suggested that the recognition of LASH as hazardous by the TCLP places it (the TCLP) at a disadvantage as an appropriate tool of assessing the success of S/S in this particular area, unless the test is modified to address this situation.

A modified DIN 418 test performed on synthol gunk (10 water to 1 solid instead of the normal 20 water to 1 solid) indicates that synthol gunk is actually the least hazardous waste material compared to LASH, GASH and GLASH with regard to trace element leachability. Only Mn came out as a concern in gunk.

CHAPTER FIVE

5. PLANT GROWTH EXPERIMENTS: EFFECT OF ASH-STABILISED ORGANIC SLUDGE ON BIOMASS PRODUCTION OF MAIZE

5.1 Introduction

The preceding chapter has been addressing the potential contamination of the environment by hazardous constituents that may leach from the stabilised waste material. While this is a formally accepted risk based approach to waste management, it says little about what is likely to happen in case of actual contamination.

There are many processes operating within the soil matrix (which is the immediate recipient environment towards groundwater contamination) that may have an effect on the migrating waste constituents. While the classification procedure outlined in the Minimum Requirements document attempts to quantify the potential impact of waste on the environment, actual studies of plant response to contamination provide a chance to observe the effects of contamination on flora.

Soil parameters such as soil pH, clay content, cation exchange capacity and, especially in the current study, carbon content may play an important role to the fate of pollutants and, consequently, to the severity of their impact on plants.

The problem with these types of studies is the large number of variables that can affect the final result of an experiment. One such variable is the action of biological processes within the soil matrix. The organic material, such as synthol gunk, can be broken down by micro-organisms in the soil. If this process is very slow, it may take a long time to fully realise the impact of synthol gunk, which may be positive or negative, in that particular environment.

Realising that a plant response study a study topic on its own, this chapter was, therefore, limited on studying the effects of synthol gunk on biomass production of maize. The aim was to determine the threshold loading rate of synthol gunk that result in a visible plant response pattern and compare it to that of the stabilised synthol gunk as a way of assessing stabilisation.

5.2 Sampling and analytical methods

5.2.1 Soil sampling

A sample of subsoil was collected for the study of plant response to contamination by Ash, GASH and synthol gunk. A subsoil sample was collected because it is subsoils are normally less leached compared to topsoils. It is also where plant roots are situated, suggesting nutrient enrichment.

The sampling area is situated in the Western Cape Province, South Africa. The sample was collected from the side of a road cutting between Hout Bay and Llundudno (Figure 5-1).

Figure 5-1: The sampling area of the soil used for the study of the effects of waste material on biomass production of maize.

Some of the exposed soil section was removed before sampling however, there still remain a possibility that the sample was slightly exposed and may have been slightly leached. The subsoil was sampled with a shovel and kept in closed plastic bags until commencement of experimental work.

5.2.2 Soil preparation

The soil was crushed using a stone on the roof of the Geological Sciences building and left to air dry for a day. The crushed soil was sieved through a 2 mm sieve. The sieved soil was subsequently used for experimental work.

5.2.3 Determination of field capacity

The determination of field capacity was conducted using a variety of soil and waste combinations to account for the possible variations in the water holding capacity of the soil when it is mixed with foreign materials. The field capacity was calculated from the saturated paste extracts of a) an unadulterated soil sample, b) a soil sample containing approximately half the highest allowed dose of each waste material and c) a soil sample containing the highest allowed dose of each waste material. The dose of each waste material per soil sample, as given in Table 5-1 in percent waste addition, was used to calculate field capacity per waste addition. From this, it was deduced that a field capacity of 100 would be adequate for the plant growth experiment.

Table 5-1: Amounts of distilled water required to achieve a saturated paste for the determination of the field capacity

	% GASH		% Ash		% Gunk		
Sample	**10**	**30**	**8.4**	**25**	**2.5**	**5**	**Control**
Distilled water (ml)	197	186	209	215	214	210	207

5.2.4 Mixing

The soil was mixed with GASH in ratios 0%, 2.6%, 5%, 10%, 15%, 25%, and 30% GASH by weight. The total mass of the mixture per pot was 500g. In order to determine the individual effects of Ash and synthol gunk on plant growth, separate experiments were conducted in which these two waste materials were added to soil and treated in the manner similar to GASH containing soil samples. The amounts of Ash and synthol gunk added to each pot were determined according to the fraction of each waste material present in a given percentage of GASH, as shown in Table 5-2.

Table 5-2: Mixing ratios of GASH, Ash and Gunk with soil for the plant growth experiment

Soil (g)	*GASH (g) (%)*	*Soil (g)*	*Gunk (g) (%)*	*Soil (g)*	*Ash (g) (%)*
500	0 (0)	500	0 (0)	500	0 (0)
487	13 (2.6)	498	2 (0.4)	489	11 (2.2)
475	25 (5)	496	4 (0.8)	479	21 (4.2)
450	50 (10)	492	6 (1.2)	458	42 (8.4)
425	75 (15)	487	13 (2.5)	437	63 (12.6)
375	125 (25)	479	21 (4.2)	396	104 (20.8)
350	150 (30)	475	25 (5)	375	125 (25)

5.2.5 Preparation of the N, P and K nutrient solution

An N, P and K nutrient solution was prepared by dissolving NH_4NO_3 (7.15g), $NaH_2PO_4 \cdot 2H_2O$ (2.52g) and KCl (2.86g) and making it up to 500 ml with distilled water in a volumetric flask. Ten millilitres of this solution were diluted to 100ml with distilled water to prepare the field capacity solution. The resulting solution was added to 500g of the soil sample as field capacity water content. This solution contained 100mgN/kg soil, 20mgP/kg soil and 60mg K/kg soil.

5.2.6 Potting and watering

The maize was washed in water to remove any preservative and was then soaked in warm water for 24 hours without any heating device. Five seeds per pot were planted at a depth of 1cm. The weight of each pot was recorded and maintained throughout the watering process. A 10% increase in the volume of water added to each pot was effected after about 10 days to account for the added mass of plants.

After planting of the seeds, the pots were taken to the phytotron unit in the Botany Department at the University of Cape Town and kept for 20 days, after which they were harvested. The phytotron unit was programmed for a 14 hour day with a maximum light intensity of 410 to 450 μ mol/m^2/s.

5.2.7 Harvesting and soil analysis

The plants were harvested by cutting with a sharp knife approximately 1 cm from the soil surface. The weight of the pot before and after harvesting was compared to determine the wet mass of the plants from each pot. The leaves were transferred to brown paper bags

for drying. The leaves were dried at 70°C for 3 days, after which the dry biomass production was recorded.

Roots were removed from the soil and the soil from each pot was air dried for a day to allow for further analysis. Each dry soil sample was crushed and sieved through a 2 mm sieve. A sample of the sieved soil (10g) was mixed with distilled water (25ml) to form a suspension. The resulting suspension was shaken for an hour in an orbiting shaker and centrifuged at 6000g for 20 minutes. The pH and electrical conductivity measurements were made and the extracts were filtered through a 0.45µm filter. An IC analysis was conducted on selected samples.

A sub sample of soil was submitted to the Agricultural Research Council for the analysis of P, K and exchangeable cations (Ca, K, Ca, Mg), Cu, Zn, Mn and B as well as the carbon content.

5.3 Results and Discussion

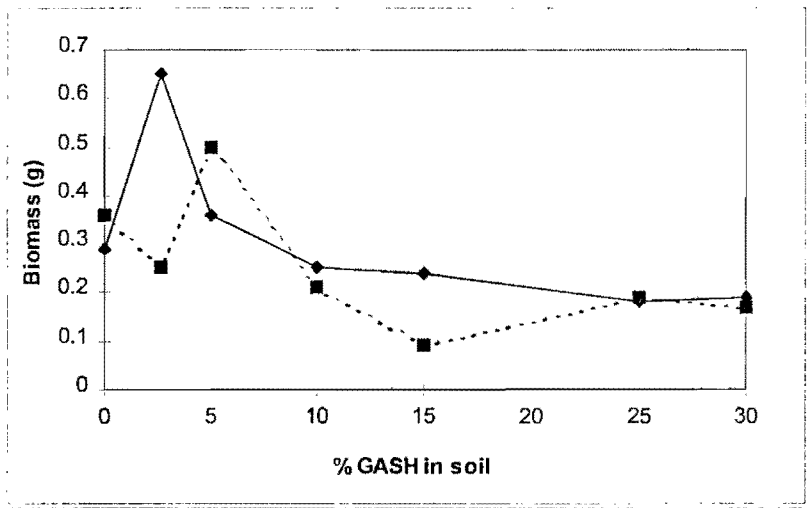
According to Figure 5-2, the ash appears to have the least effect on biomass production of the test plants. There seems to be an increase in biomass production at 2.2% and 4.2% Ash, but due to the scope of this study, it was not possible to identify the cause. It may however, be due to either the introduction of nutrients contained in Ash (which will probably be below toxic levels at low Ash additions) or experimental error.

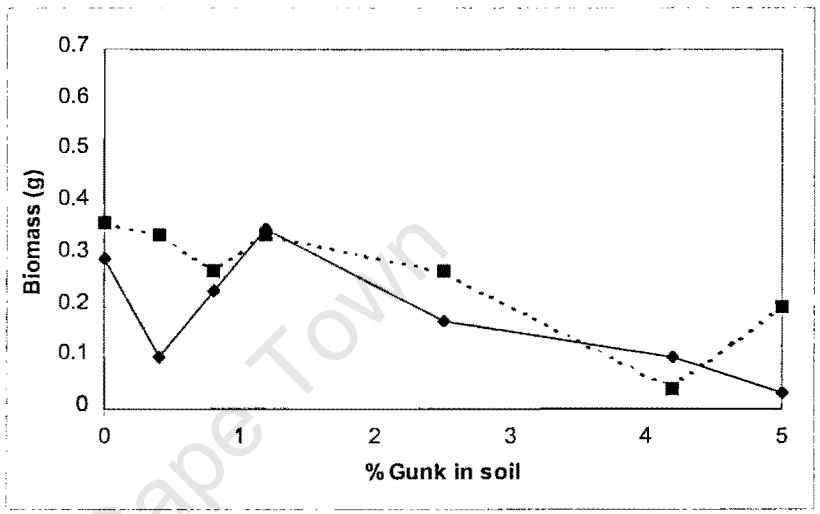
Synthol gunk appears to have a significant effect on plants at additions above 2.5%. Synthol gunk duplicates at 0.4% addition appear to be in disagreement with one sample showing a significant decline in plant growth while the other shows a slight decline It was noticed that during the study some seeds had difficulties with germinating which, apart from genetic variations, could be due to either toxic components from the waste material or the smectitic nature of the soil. The soil had a tendency to shrink and swell. The crust formed when it dries out was found to be strong enough to block any movement through the soil, this may have played a role in some plants having difficulty in germination. A similar disagreement in 2.6% GASH duplicate is observed and may be due to similar reasons as the discussed above. Addition of more than 0.8% synthol gunk in soil results in a constant decline in biomass production, suggesting a negative effect on plant growth.

Comparison of relative plant growth response between different treatments (GASH, Ash and

synthol gunk) shows that at lower waste additions (below 10% GASH, 1.2% Gunk and 8.4% Ash), plants grown in synthol gunk treated soil show more detrimental effects with regard to plant growth. GASH on the other hand shows negative effects when added above 10%.

Photographs shown in Figure 5-3 were taken after the maize has been allowed to grow for 19 days. A shallow decline in biomass production can be observed on the soil treated with Ash.. Soils treated with synthol gunk and GASH show relatively steeper decline in biomass production.





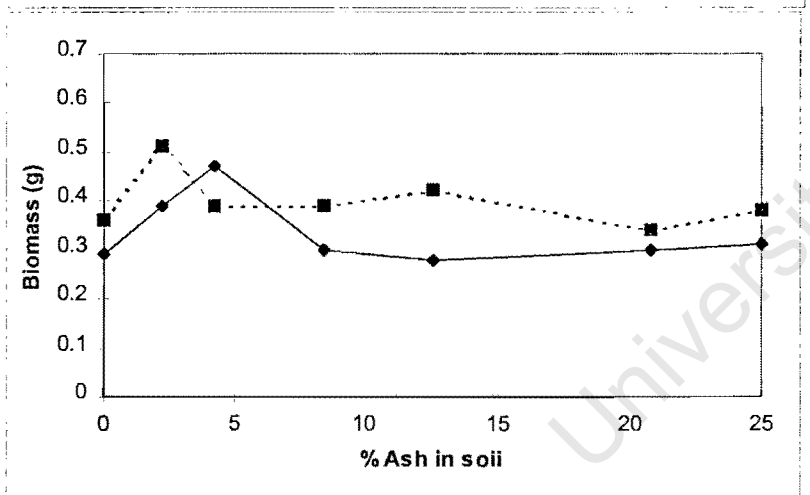


Figure 5-2: Biomass production of maize treated with GASH, Gunk and Ash. Duplicate results plotted on the same system of axes.

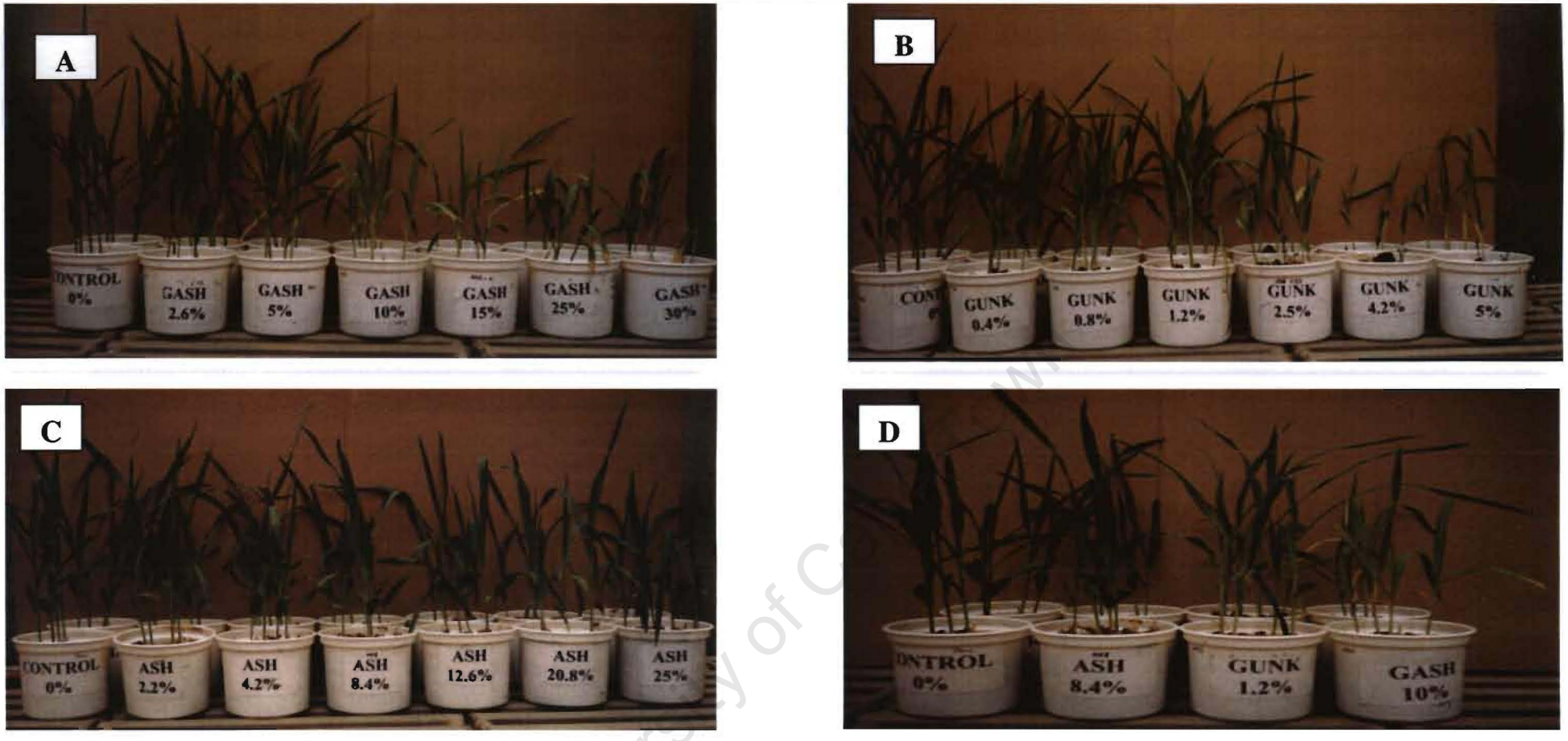


Figure 5-3:Photographs of the test plants taken after 19 days showing effect of A) GASH, B) Gunk and C) Ash on plant growth response. A comparison D) of 8.% Ash, 1.2% Gunk, 10% GASH with the control is also shown.

A comparison of the control experiment with pot containing soils treated with 8.4% Ash, 1.2& synthol gunk and 10% GASH is shown in Figure 5-3D. It should be emphasised that a 10 GASH mixture is composed of approximately 8.4% Ash and 1.2% synthol gunk, hence the comparison in Figure 5-3 D. This photo suggests that a mixture of synthol gunk and Ash can have a more undesirable effect on plants that the Ash and synthol gunk on their own.

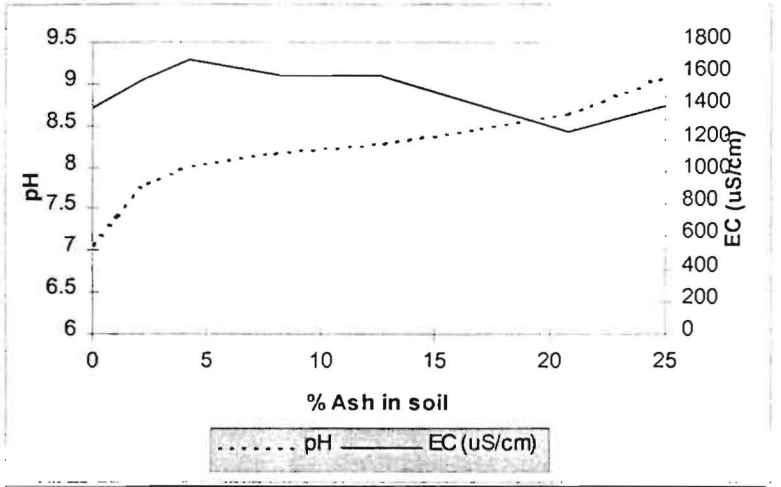
The observed toxicity of Ash, GASH and synthol gunk appear to be consistent with variations in the electrical conductivity of the soil extracts presented in Figure 5-4. Ash treated soil shows a net shallow decline in EC which is consistent with the slight decline in biomass production observed in Figure 5-2. Soil treated with synthol gunk shows a relatively stable pH throughout the treatment range, but the EC decreases as more synthol gunk is added to soil. This EC decrease is consistent with the observed decline in biomass production associated with the presence of synthol gunk in the soil. The decrease in electrical conductivity of GASH treated soil also shows similarity to the effect of GASH on biomass production.

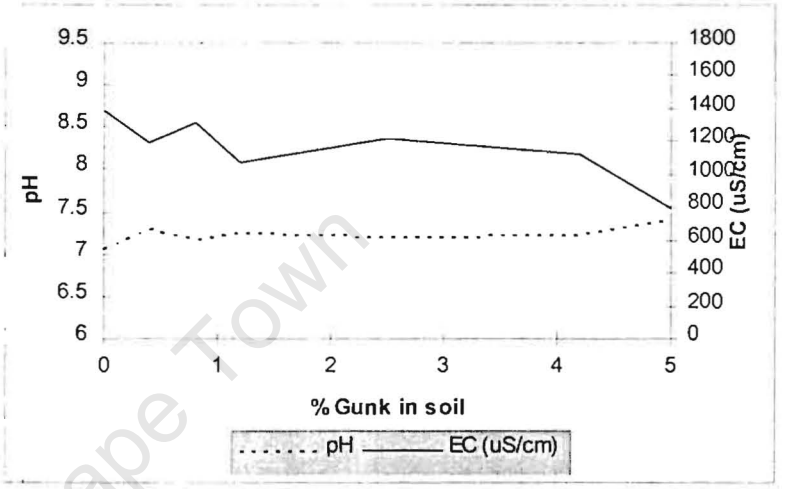
No trend could be identified on the elemental analysis of major ions given in Table 5-3. While there are some variations in the ionic composition of the extracts at different percentages of waste addition, there seem to be no definite pattern associated with them.

Table 5-3: Major cations and anions of selected soil samples from the plant growth tests.

		% GASH			% Ash			% Gunk		
Analysis (ppm)	**Control**	**2.6**	**15**	**30**	**2.2**	**8.4**	**25**	**0.4**	**1.2**	**5**
pH	7.07	8.01	8.54	8.63	7.78	8.19	9.06	7.30	7.27	7.43
EC (µS/cm)	1392	1469	669	509	1570	1589	1409	1194	107 2	793
Na	152	185	202	132	172	194	193	157	155	156
NH_4	2.6	2.2	3.6	2.4	2.9	1.8	2.8	2.2	1.3	2.8
K	2.9	3.7	4.6	3.1	3.2	2.5	3.7	2.1	2.5	4
Mg	10	10	18	13	14	15	10	9.5	7.7	3.4
Ca	37	64	69	61	46	67	N/A	42	52	141
F	0	0	0.22	0.85	0.41	0.26	0.15	0	0	0.14
Cl	194	177	60	137	195	232	139	186	190	243
Br	0.94	1	0	0.98	2.6	1.7	0	1.6	1.5	1.7
NO_3	31	22	0.52	1.4	33	44	21	21	22	4.4
SO_4	36	60	35	98	61	128	118	44	43	81

N/A = results not available





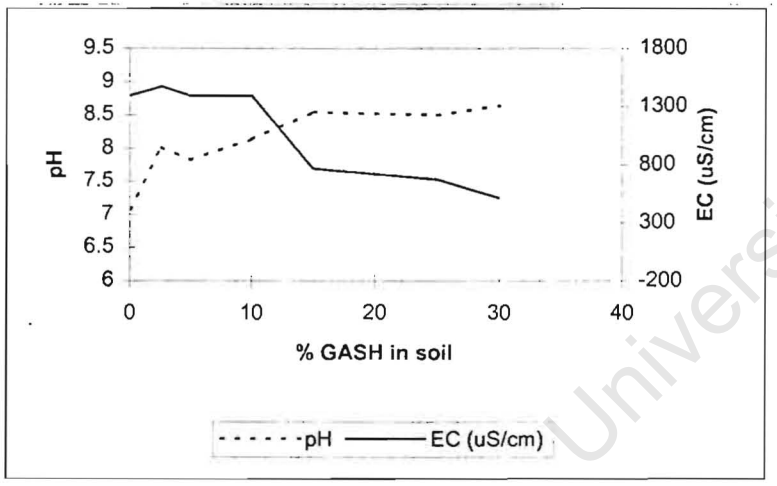
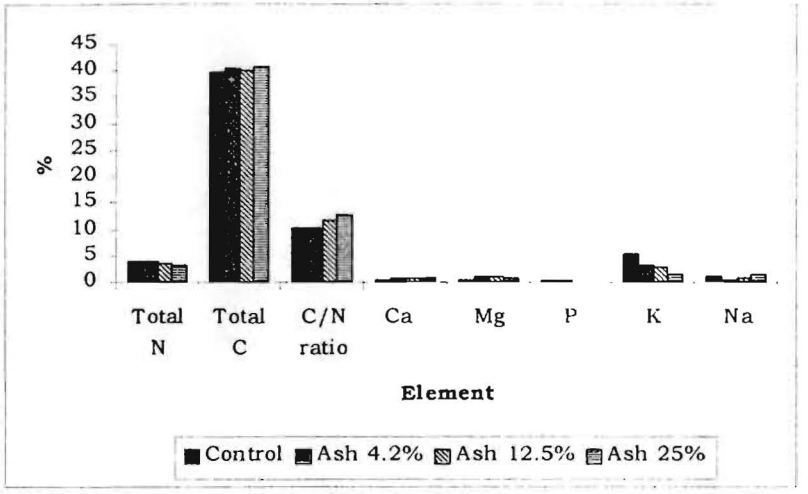
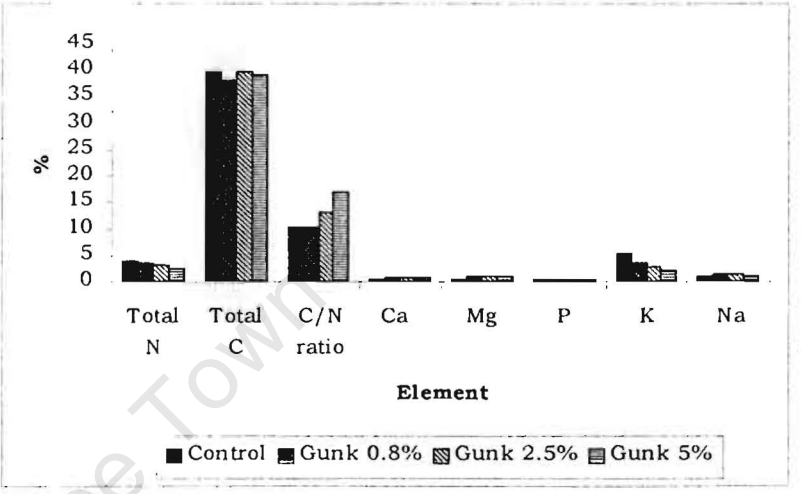


Figure 5-4: The pH and EC of soil extracts (1 part solid to 2.5 parts water) of the soils used for the plant growth response experiment.





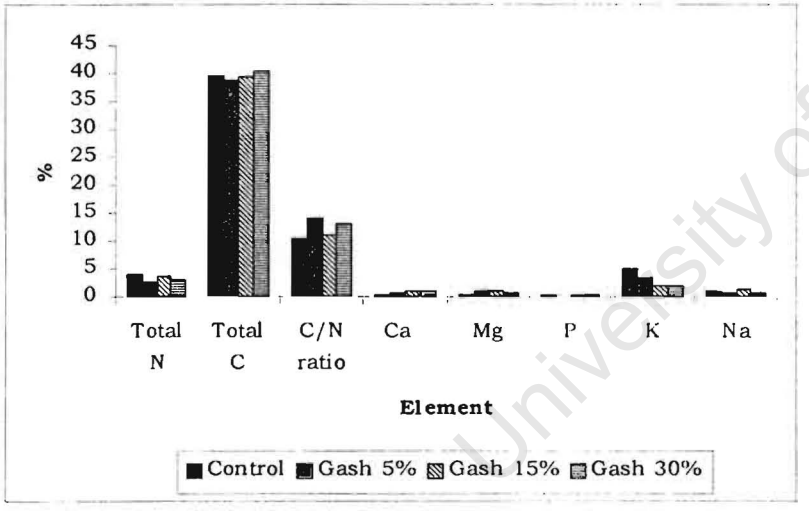
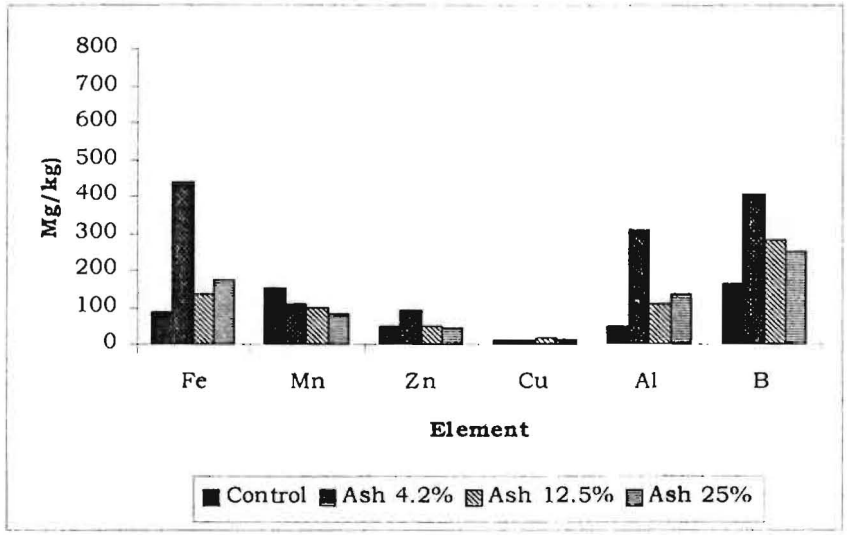
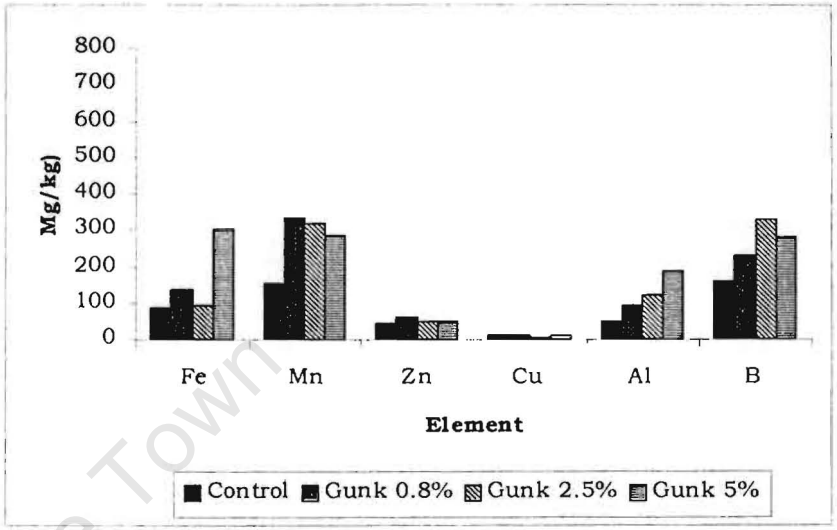


Figure 5-5: Foliar analysis showing the uptake of major constituents by plants, dry mass





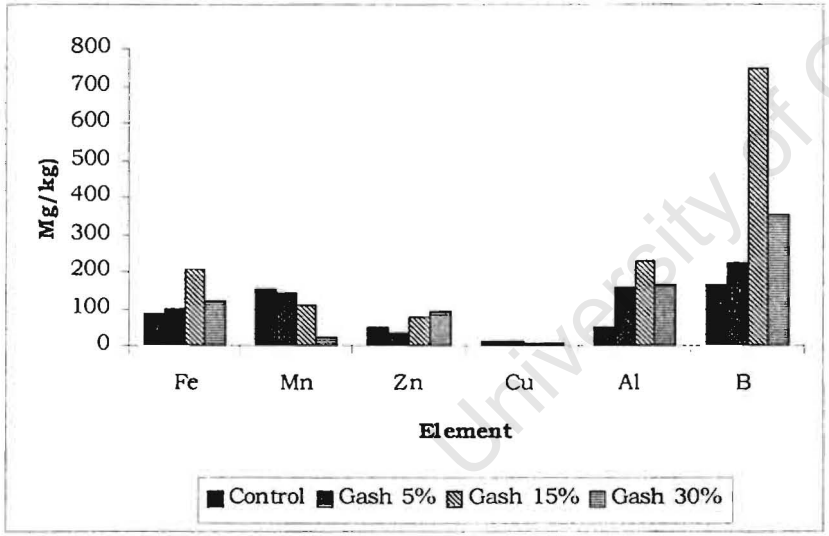


Figure 5-6: Foliar analysis showing the uptake of tracc clements by plants, dry mass

When plants were grown on synthol gunk and ash treated soils, very slight variations in nutrient uptake were observed. Potassium uptake appeared to be inhibited by the addition of foreign material into the soil, even fine ash (Figure 5-5). Perhaps it should be noted that the cation exchange capacity of fine ash is likely to be very different from that of the soil. This may be due to a number of factors such as the mineral composition of ash relative to that of the soil, the effective radius of the charge site and the effect of entropy on the exchange reactions (McBride, 1994).

The addition of synthol gunk to soil also appeared to reduce K uptake, while Na uptake remained relatively constant. An increase in the C/N ratio uptake was observed when the synthol gunk addition to soil was increased. But this appears to be caused by a decrease in nitrogen uptake by the plants, rather than increased carbon uptake. Plants grown on soil with treated gunk (GASH), however, did not exhibit a decrease in N uptake.

The uptake of trace elements by plants was found to generally increase with addition of foreign material to soils. Notably, the increase in Mn uptake when untreated synthol gunk was added to soil was not observed when treated gunk (GASH) was used instead (Figure 5-6). Iron, Al and B (and Zn to a lesser extent) were found to significantly concentrate in plant tissue with the addition of 4.2% fine ash into the soil.

A similar effect is observed when 15% of treated gunk is added to soil. Boron uptake was especially significant (increases from 161 mg/kg to 744 mg/kg, a 4.5 fold increase in uptake). Unfortunately, an examination of the trace element uptake data with the biomass production data did not reveal any correlation between the two sets of data.

A white efflorescence was observed on the surface of pots containing synthol gunk and GASH during watering. It is possible that the efflorescence was chiefly composed of gypsum due to its lack of taste and its white colour. These salts making up the efflorescence are not likely to be available for plant growth. It may be possible that the formation of efflorescence contributes to the negative impact on plants observed with synthol gunk and GASH. Ash showed reduced toxicity compared to the other waste materials while Ash treated soil exhibited no efflorescence.

It is suggested that as a future work initiative, it may be worthwhile to separate the top part of the soil from the bottom part and analyse them separately to study the effects of this salt partitioning in plant growth.

5.4 Conclusion

Ash and GASH show stimulation of plant growth when added to soil at concentrations not exceeding 5% addition by weigh. However, while addition of Ash to soil result in a gradual and shallow decline in biomass production of maize, GASH treated soil starts showing significant effects on plant growth at GASH additions of about 10%. While synthol gunk treated soil starts showing negative effects at additions above 2.5%, addition of 4.2% synthol gunk to soil results in worst plant growth inhibition and no stimulation is observed at any concentration. It can be concluded that the stabilisation of synthol gunk using Ash results in a mixture with a potential to be a plant growth stimulant, possibly as a trace element and carbon source, at low concentrations (less than 5% at a mixing ratio of 1 part synthol gunk to 5 parts Ash). Excessive addition of this stabilised material to soil can, however, have detrimental effects to plant life. Results of this study should be taken with caution since plant growth studies need much more time to be conclusive. Parameters such as effect on crop yield, effects on the next generation crops as well as long term effects on soil structure require much more in depth studies which could not be covered in this study.

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7. APPENDIX

7.1 Instrumental parameters

7.1.1 XRD

Instrument	Philips PW 1390 diffractometer
X-ray tube	PW2233 Cu NF (Kα = 1.54 Å)
Accelerating voltage	40kV
Beam current	25 mA
Range	5 to 65° 2θ
Step size	0.1° 2θ
Counting time	1 second per step

7.1.2 Particle size analysis

Instrument	Malvern Mastersize High Resolution Particle Size Analyser
Analysis model	polydisperse
Pump	70%
Stirrer	70%
Input density	3 g/cm^3
Range lens	1000 mm
Beam length	2.4 mm
Sampler	MS17

7.1.3 WDXRF

Instrumental parameters for the WDXRF are described in detail by Willis (1996).

7.1.4 XRD data

Table 7-1: d-spacings and relative intensities of peaks from Ash.

d-spacing (Å)	*Relative intensity (%)*	*Angle (°2θ)*
5.37	6.67	16.49
4.25	13.26	20.88
3.34	100	26.67
3.21	2.14	27.77
3.03	17.51	29.45
2.88	5.36	30.98
2.54	11.49	35.34
2.45	16.57	36.59
2.33	4.17	38.52
2.83	9.24	39.42
2.2	13.71	40.94
2.12	17.39	42.57
1.98	4.64	45.79
1.87	6.1	48.59
1.82	11.24	50.19
1.67	3.38	55.04
1.6	8.03	57.62
1.54	13.11	60.03
1.54	13.11	60.03
1.52	12.34	60.73

Table 7-2: d-spacings and relative intensities of peaks from LASH.

d-spacing (Å)	*Relative intensity (%)*	*Angle (°2θ)*
7.96	4.76	11.12
4.9	22.15	18.1
4.26	16.12	20.86
4.04	1.68	21.96
3.84	5.97	23.14
3.34	100	26.67
3.03	46.43	29.44
2.62	43.01	34.17
2.54	16	35.3
2.45	14.29	36.59
2.28	23.02	39.43
2.2	15.81	40.9
2.13	8.06	42.5
2.11	7.69	42.86
1.92	18.56	47.24
1.87	9.94	48.54
1.82	22.63	50.18
1.79	20.72	50.87
1.67	12.13	54.94
1.6	9.54	57.53
1.54	14.1	59.97
1.52	12.61	60.72
1.48	4.6	62.65